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Separation of Biomass Components by Membrane Filtration

Process Development for Hemicellulose Recovery

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2013

LUND
UNIVERSITY

Academic thesis which, by due permission of the Faculty of Engineering of Lund University will be publicly defended on 20 September 2013 at 13.15 in Lecture hall K:B at the Centre for Chemistry and Chemical Engineering, Getingevägen 60, Lund, for the degree of Doctor of Philosophy in Engineering.

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Separation of Biomass Components by Membrane Filtration
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Abstract

One of the major challenges facing the world today is the reduction of our dependency on fossil resources as their exploitation has severe negative effects on the environment. One way of realizing this is to utilise the components of lignocellulosic biomass to a greater extent as feedstock for various industrial products. However, such utilisation requires the extraction of the biopolymers from their native structure, followed by efficient isolation from the complex extraction solution. The aim of this work was to develop processes that can be used on a large scale for the separation and recovery of biomass components from various kinds of industrial process streams.

In the first part of this work, a membrane-based separation process was developed that allows the fractionation of biomass components in two different process waters originating from mechanical pulp production. Filtration and membrane filtration were optimised in order to obtain concentrated fractions of wood fibre residues, suspended/colloidal matter, hemicelluloses and lignin. The most valuable fraction obtained from this process was the ultrafiltration retentate, containing up to 64 g/l of hemicelluloses at a purity of about 60%. Furthermore, the process generated a purified water stream that could be reused in the pulp mill. Using enzymatic treatment, it was possible to cross-link hemicelluloses in pulp mill process water, thereby increasing their molecular mass. Subsequent ultrafiltration was shown to partly separate hemicelluloses with high molecular mass from those with low molecular mass. This approach could be of interest in cases where large hemicelluloses with a narrow size distribution are needed for the manufacture of bio-based products.

The major objective in the second part of the work was to recover hemicelluloses from a high-viscosity solution obtained after alkali extraction from wheat bran. Hemicelluloses were separated from the extraction chemical (sodium hydroxide) using a ceramic ultrafiltration membrane with a cut-off of 10 kDa. Only a moderate flux was achieved (up to 75 l/m^2h) by optimising the operating conditions. However, flux could be increased substantially (to 225 l/m^2h) by the introduction of dead-end filtration prior to ultrafiltration. It was also shown that the extraction chemical could be recovered from the ultrafiltration permeate by nanofiltration. An extremely high flux and good removal of organic impurities (lignin, sugars) were achieved with the polymeric nanofiltration membranes NP010 and MPF-36. Preliminary cost estimates revealed that the investment in a nanofiltration plant would be paid back after only 1150 h of operation.

Populärvetenskaplig sammanfattning

De flesta produkter som vi dagligen använder tillverkas genom att utnyttja fossila råvaror som olja, kol och naturgas. Ett stort problem är att dessa råvaror bara finns i begränsade mängder i naturen, vilket medför att de förr eller senare tar slut. Dessutom medför förbränning av fossila råvaror att det bildas miljöskadande gaser (t.ex. koldioxid) som ansamlas i atmosfären och bidrar till den globala uppvärmningen. För att begränsa miljöbelastningen är det därför viktigt att vi minskar användningen av fossila råvaror i framtiden genom att istället använda förnyelsebara material som biomassa i större utsträckning.

Biomassa (t.ex. skogs- och jordbruksprodukter) innefattar allt organiskt material som bildas i naturen och består huvudsakligen av tre komponenter: cellulosa, hemicellulosa och lignin. Under de senaste åren har man gjort stora framsteg för att ta fram tekniker för tillverkning av värdefulla produkter ur biomassas olika komponenter. Till exempel är det idag möjligt att tillverka bioetanol från cellulosa, vilket är ett miljövänligt bränsle för våra bilar. Hemicellulosa kan användas som utgångsmaterial till barriärfilmer som kan ersätta plast och aluminium i livsmedelsförpackningar. Även för lignin har forskare hittat mycket intressanta tillämpningar. Lignin har visat sig att vara ett utmärkt fast biobränsle och kan också användas för att tillverka kompositmaterial och kemikalier.

Även om det finns flera alternativa möjligheter att använda biomassa, så är detta tyvärr inte alldeles enkelt. Cellulosa, hemicellulosa och lignin är i biomassa bundna till varandra och bildar där ett stabilt nätverk. Man måste därför behandla biomassan på något sätt för att bryta upp nätverket och göra komponenterna tillgängliga. I många industriella processer uppnås detta genom att behandla biomassan vid hög temperatur och högt tryck, eller genom att använda starka kemikalier. Då bildas vätskor som å ena sidan innehåller relativt stora mängder värdefulla biopolymerer, men å andra sidan också en hel del oönskade föroreningar. Förutsättningen för att kunna använda de tillgängliga biopolymererna till nya produkter är att man kan rena upp dem genom att skilja dem från varandra och från föroreningarna. Men än så länge saknas det bra processer för detta ändamål. Målsättningen med mitt projekt var därför att utveckla lämpliga separationsmetoder som gör det möjligt att utvinna biomassas komponenter från industriella vätskor på ett kostnads- och energieffektivt sätt.

Jag har i mitt arbete huvudsakligen använt en separationsteknik som kallas för membranfiltrering. I denna teknik använder man ett tätt filter i vilket det finns hål (porer) som är så små att de inte ens kan ses med blotta ögat. Genom att man väljer membran med lagom stora hål, kan man samla de olika biopolymererna i separata fraktioner och dessutom plocka bort föroreningarna. Men att skilja många substanser i en vätska från varandra är komplicerat. Det kan behövas flera på varandra följande steg, med olika membran i de olika stegen. Dessutom är det mycket viktigt att man väljer rätt driftsbetingelser när man använder sig av membranfiltrering. Till exempel är membranets prestanda beroende av vätskans temperatur, tryckskillnaden mellan membranets båda sidor (transmembrantryck) och vätskans hastighet vid membranytan (tvärströmshastighet). För att försvåra det ytterligare kan man inte använda samma parametrar för alla vätskor, utan de måste anpassas specifikt för varje enskild tillämpning.

Jag har i mitt doktorandarbete i detalj studerat vilka steg som behövs och vid vilka driftsbetingelser det går bäst att utvinna biopolymererna (framför allt hemicellulosa) från olika industriella vätskor. Tre olika företag har försett mig med processvätskor och i avhandlingen diskuterar jag upparbetningsstrategier för dessa vätskor baserade på membranfiltrering. Från min synpunkt var det viktigast att få ett så högt utbyte som möjligt av de värdefulla biopolymererna, att göra processen kostnads- och energieffektiv samt att processen kan tillämpas i industriell fullskala.

List of publications

This thesis is based on the following papers, which will be referred to in the text by their roman numerals. The papers are appended at the end of the thesis.

I. Persson, T., **Krawczyk, H.**, Nordin, A.-K. and Jönsson, A.-S.
Fractionation of process water in thermomechanical pulp mills. *Bioresource Technology*, 2010, 101(11), 3884-3892.

II. **Krawczyk, H.** and Jönsson, A.-S.
Separation of dispersed substances and galactoglucomannan in thermomechanical pulp process water by microfiltration. *Separation and Purification Technology*, 2011, 79(1), 43-49.

III. **Krawczyk, H.**, Oinonen, P. and Jönsson, A.-S.
Combined membrane filtration and enzymatic treatment for recovery of high molecular mass hemicelluloses from chemithermomechanical pulp process water. *Chemical Engineering Journal*, 2013, 225, 292-299.

IV. **Krawczyk, H.**, Arkell, A. and Jönsson, A.-S.
Membrane performance during ultrafiltration of a high-viscosity solution containing hemicelluloses from wheat bran. *Separation and Purification Technology*, 2011, 83, 144-150.

V. **Krawczyk, H.**, Arkell, A. and Jönsson, A.-S.
Impact of prefiltration on membrane performance during isolation of hemicelluloses extracted from wheat bran. *Separation and Purification Technology*, 2013, 116, 192-198.

VI. Arkell, A., **Krawczyk, H.**, Thuvander, J. and Jönsson, A.-S.
Evaluation of membrane performance and cost estimates during recovery of sodium hydroxide in a hemicellulose extraction process by nanofiltration. *Separation and Purification Technology*, 2013, *(Accepted)*

My contribution to the publications

I. I planned and carried out the experimental work together with Tobias Persson and Anna-Karin Nordin. I was involved in writing the article.

II. I planned and carried out all the experimental work. I wrote the article.

III. I planned and carried out all the experimental work apart from the enzymatic treatment, which was performed by Petri Oinonen. I wrote the article.

IV. I planned and carried out the experimental work together with Anders Arkell. Our industrial partner produced the hemicellulose extract. I wrote the article.

V. I planned the study together with Anders Arkell, and carried out part of the experimental work. Johan Thuvander and Filip Vrgoc performed most of the ultrafiltration studies under my and Anders Arkell's supervision. Our industrial partner produced the hemicellulose extract. I wrote the article.

VI. I planned the study together with Anders Arkell, and performed a large part of the cost calculations. Johan Thuvander carried out most of the experimental work under my and Anders Arkell's supervision. I wrote the article together with the other authors.

Other related publications

Krawczyk, H., Persson, T., Andersson, A. and Jönsson, A.-S.
Isolation of hemicelluloses from barley husks.
Food and Bioproduct Processing, 2008, 86(C1), 31-36.

Roos, A., Persson, T., **Krawczyk H.**, Zacchi, G. and Stålbrand, H.
Extraction of water-soluble hemicelluloses from barley husks.
Bioresource Technology, 2009, 100(2), 763-769.

Krawczyk, H. and Jönsson, A.-S.
The influence of feed flow channel diameter on frictional pressure drop, membrane performance and process cost in full-scale tubular ceramic membranes.
Chemical Engineering Research and Design, 2013, *(Accepted)*

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Abbreviations and symbols

Abbreviations

CTMP	Chemithermomechanical pulp
TMP	Thermomechanical pulp

Symbols

A	Filtration area
C	Concentration
J	Permeate flux
k	Mass transfer coefficient
ΔP	Pressure difference across the membrane or the filter cloth
R_c	Hydraulic resistance of the filter cake
R_m	Hydraulic resistance of the membrane or the filter cloth
R_{obs}	Observed retention
R_{tr}	True retention
t	Time
t_{forw}	Forward filtration time
t_{pulse}	Pulse length
V	Volume
VR	Volume reduction
Y	Yield, recovery
α	Specific resistance of the filter cake
κ	Concentration parameter
η	Dynamic viscosity
$\Delta\pi$	Osmotic pressure difference across the membrane

Subscripts

0	Initial state
b	Bulk
f	Feed
m	At membrane surface
p	Permeate
r	Retentate

Contents

Chapter 1

Introduction

1.1 Background

The utilisation of fossil resources such as oil, coal and natural gas is one of the major reasons for the high standard of living in many parts of the world. Almost all fuels, materials and chemicals used in everyday life have, until now, been produced to a greater or lesser extent from fossil resources. However, this is not sustainable in the long term. Fossil resources are decreasing, and will soon be depleted if their exploitation is not considerably reduced. Furthermore, the combustion of oil, coal and natural gas leads to the emission of carbon dioxide and other greenhouse gases, which are associated with shifts in the global climate. There is strong evidence that the increase in the average temperature on Earth, of 0.74°C within the last century, is the consequence of the increased use of fossil resources, and the rise in temperature is expected to be even greater in the coming century (1.1 to 6.4°C) [1]. It is thus clear that industrial and fuel needs must be made less dependent on fossil resources, for example, by increasing the use of renewable materials such as lignocellulosic biomass as a feedstock for industrial products.

Although some products are already made from lignocellulosic biomass, its full potential as a resource for bio-based products has not yet been realized. Among the major components of biomass, cellulose is the only one that has found widespread applications as an industrial feedstock. This polysaccharide has been used for more than a century, for the manufacture of various paper qualities in the pulp and paper industry, and it is also a suitable raw material for the production of textiles [2]. In the near future, cellulose from lignocellulosic biomass is expected to play an important role as a feedstock for renewable transportation fuels such as bioethanol [3, 4], and it has also shown great promise for use in high-performance materials such as cellulose nanopaper films [5]. The other two main biomass components, hemicelluloses and lignin, are far from being fully exploited for commercial products, although possible future applications have been identified. Research has shown that hemicelluloses have suitable properties for use in renewable barrier films [6–8], coatings [7] and hydrogels [9, 10]. Other suggested applications are as additives during paper making [11, 12] and as health food ingredients due to the prebiotic properties of certain hemicelluloses [13]. Lignin, being a macromolecule with a relatively high caloric value and physical strength, could have a future as a renewable fuel [14], as a dispersant for ceramics and clays [2], and as a feedstock in the manufacture of construction materials such as carbon fibres [15].

A major obstacle to the increased utilisation of biomass is the fact that biomass components are only rarely easily available. In their native forms, cellulose, hemicelluloses and lignin are embedded in a rigid structure, and they must first be released using treatment with chemicals or heat. This is done in many processes in the bio-based industry, creating process streams in which valuable biomass components are dissolved together with other co-extracted substances, and sometimes extraction chemicals. The use of biopolymers in these mixtures as feedstock for bio-based products is obviously only feasible if they can be efficiently recovered. However, until now, there has been little development of cost-efficient separation processes for this purpose, and thus more research is required on the separation of biomass components. As membrane filtration requires a relatively low energy input, is highly selective, and allows separation without the addition of chemicals, this technique is expected to play an important role in the separation of biopolymers.

It may be possible, in the future, to exploit all the components of biomass through the development of processes designed to separate and utilise lignocellulosic biomass. One possible way of utilising biomass is illustrated in Figure 1.1. Hemicelluloses and lignin with high molecular mass can, for example, be extracted from biomass by appropriate pretreatment. Both biopolymers can then be purified and concentrated using membrane filtration, and subsequently used for the manufacture of high-value products. The cellulose in the solid fraction remaining after pretreatment can be hydrolysed to sugars and fermented to ethanol, providing a source of biofuel after distillation. The lignin in the stillage after distillation could also be utilised, for example, as a fuel or chemical. The conversion of the entire raw material into products with large diversity is often referred to as a biorefinery.

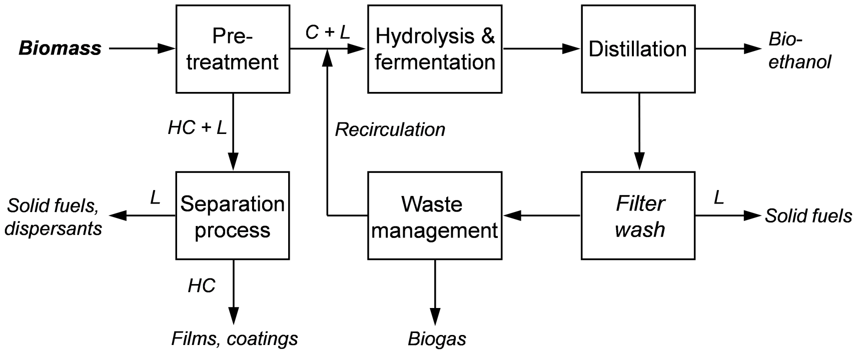

Figure 1.1: Example of future biomass utilisation in a so-called biorefinery. The abbreviations C, HC and L denote cellulose, hemicelluloses and lignin. (Adapted from Hahn-Hägerdal et al. [3])

1.2 Aims and outline of this thesis

The major objective of this work was to develop separation processes that can be applied on a large scale for the recovery of valuable biopolymers, in particular hemicelluloses, from process streams in the bio-based industry. Membrane filtration was used in these processes, and the effects of factors such as the type of membrane, the operating conditions and the process configuration on the membrane performance were investigated. Process streams containing biopolymers originating from wood or agricultural residues were used in the experimental studies. Hence, this work also covers the influence of the properties of the solution on the separation performance.

In **Chapter 2** the origin of the biomass components cellulose, hemicelluloses and lignin is discussed, together with the chemical structure and molecule properties relevant for their separation. In **Chapter 3** processes are presented that lead to the dissolution of biomass components into a liquid phase. The most relevant processes for this work are the mechanical pulping of wood and the alkali extraction method. Membrane filtration was applied for the separation of biomass components, but conventional dead-end filtration was used for pre-filtration. Fundamental aspects of these separation techniques are described in **Chapter 4**.

The experimental work was mainly aimed at developing a separation process for process water from mechanical pulp mills. **Chapter 5** presents the results obtained during this development. The components in the process water were fractionated into purified fractions of undissolved substances (e.g. fibre residues), polymeric hemicelluloses, lignin and pure water, using a multi-stage process consisting of microfiltration, ultrafiltration and nanofiltration. The molecular mass of hemicelluloses can be increased by introducing an enzymatic treatment stage in the process, which could enhance their suitability in high-value applications.

The other process stream used in this work was alkaline extract from wheat bran; the most valuable component of which is hemicelluloses, although it also contains considerable amounts of the extraction chemical and some impurities. The results concerning the separation of the components in this kind of process stream can be found in **Chapter 6**. A major challenge during the separation of the components in alkaline extract is the high viscosity and the presence of foulants, leading to low capacity during hemicellulose recovery by ultrafiltration. Various strategies were studied to improve ultrafiltration performance, including the application of pre-filtration. Furthermore, the possibility of recovering the extraction chemical by nanofiltration was evaluated. Finally, some concluding remarks and suggestions for future studies are presented in **Chapter 7**.

Chapter 2

Lignocellulosic biomass

Biomass is available in large quantities and has the potential to become an important resource for the manufacture of biofuels, biochemicals and biomaterials. The use of biomass for such purposes is of particular interest as it offers the possibility of reducing our need for fossil resources, and thus the emission of greenhouse gases. However, in order to realize the sustainable and cost-efficient utilisation of biomass, the raw material used for bioproducts should not compete with the production of food, and should moreover be of low value. Lignocellulosic biomass, for example, the husks, straw and bran from agricultural crops and materials based on wood fulfil these requirements, and have the further advantage of being available in large quantities in agriculture and the forestry industry. Lignocellulosic biomass is therefore considered to be an excellent feedstock for future high-value bioproducts, and was the raw material studied in the present work.

In order to achieve the separation of different substances one usually takes advantage of the differences in structure and properties of the materials, such as size, charge and solubility. As the major goal of this work was to develop cost-efficient processes for the separation of components in lignocellulosic biomass, detailed knowledge concerning the structural aspects of the major biomass components is particularly important. The structure and properties of the components of biomass and the ways in which these components are interconnected in plant matter will therefore be discussed in this chapter.

2.1 The major components of biomass

Lignocellulosic biomass is mainly composed of cellulose, hemicelluloses and lignin and, to a minor extent, additional substances such as extractives, pectins, proteins and inorganic compounds (ash). The composition of lignocellulosic biomass varies markedly among plant species, and between different parts of the same plant [16]. The pulp mill process water used in the studies described in Papers I-III contained substances originating from spruce wood, while the alkaline extract used in the studies presented in Papers IV-VI was derived from wheat bran. The compositions of the major components of these two lignocellulosic materials are given in Table 2.1. In spruce, the presence of extractives should also be mentioned (∼1% of dry matter) [16], while in wheat bran proteins can be present to a considerable degree (up to 15%) [17].

Table 2.1: The major components of the lignocellulosic materials studied in this work, given as the percentage of dry solids.

Raw material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ref.
Spruce	46.5	25.1	30.9	[16]
Spruce	49.5	21.6	28.7	[18]
Wheat bran	14.8	49.7	5.3	[19]
Wheat bran	18.7	62.3	3.8	[17]
Wheat bran	25.0	45.0	6.0	[20]

2.1.1 Cellulose

Cellulose is the major component in most lignocellulosic materials. The total amount of cellulose produced every year by nature exceeds 100 billion tons [21]. Cellulose is a homopolysaccharide, composed exclusively of β-D-glucopyranose subunits. These subunits are linked together by 1,4-glycosidic linkages, forming linear cellulose chains containing typically 8000 to 15000 glucose residues (see Figure 2.1) [21]. As a consequence of the high degree of polymerisation, native cellulose has a high molecular mass. The single cellulose chains interact with each other through strong inter- and intramolecular hydrogen bonds and weak van-der-Waals forces. These interactions result in the formation of larger arrangements consisting of several cellulose molecules, in which highly ordered (crystalline) and less ordered (amorphous) regions exist [22]. These arrangements are called microfibrils, and are commonly surrounded by hemicelluloses and lignin. Microfibrils themselves interact to form fibrils, which in turn form cellulose fibres.

Due to the strong aggregation of cellulose chains in biomass, cellulose is almost insoluble in most solvents, and has a high tensile strength [22]. Furthermore, the fibrous structure and the interconnection with other biopolymers protect cellulose to some extent against acid and enzymatic degradation. However, cellulose molecules can be degraded and solubilised after disruption of the fibrous structure by pretreatment. Pretreatment and subsequent enzymatic or acidic degradation are important steps in the production of second generation bioethanol from lignocellulosic biomass [3, 18].

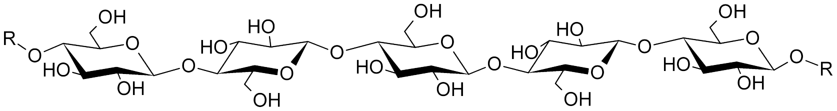

Figure 2.1: Molecular structure of cellulose.

2.1.2 Hemicelluloses

Hemicelluloses are a group of amorphous polysaccharides that have lower molecular mass, and a higher degree of branching than cellulose, and consequently higher solubility in most solvents, including water [22]. Hemicelluloses are composed of various hexose and pentose sugar residues. The most common monomeric components are D-glucose, D-mannose and D-galactose, together with D-xylose and L-arabinose. Smaller amount of D-glucuronic acid, D-galacturonic acid, 4-O-methyl-D-glucuronic acid and L-rhamnose may also be present.

Hemicelluloses are divided into the groups mannoglycans (mannans), xyloglycans (xylans), xyloglucans and β-glucans, depending on the sugar composition of the backbone of the molecule [7, 23]. Several hemicelluloses belonging to different groups can be found in the cell walls of plants. In softwood, galactoglucomannan is the principle hemicellulose, together with a minor amount of arabinoglucuronoxylan [24]. In hardwood, glucuronoxylan and glucomannan are found, the former being predominant [25]. Agricultural residues contain considerable amounts of xylan-type hemicelluloses, especially arabinoxylans [26].

Hemicelluloses are relatively stable at high pH, but the glycosidic linkages in the macromolecules are easily cleaved under acidic conditions [12, 22]. In the native form, the monomeric subunits of most types of hemicellulose are acetylated. Under alkaline conditions the acetyl groups are cleaved from the monomeric subunits [22], affecting the solubility of the molecules [12]. Details of the structure and properties of the major hemicelluloses found in spruce wood and wheat bran are presented below.

Galactoglucomannan

Galactoglucomannan is the major hemicellulose found in softwood such as spruce and pine (~20% of wood), and is also present without the galactose side groups in hardwood [22]. As shown in Figure 2.2, its backbone consists of β-D-glucopyranose and β-D-mannopyranose subunits linked together via 1,4-linkages. Residues of α-D-galactopyranose are attached mainly to the D-mannopyranose units of this backbone via 1,6-linkages, which gives the molecule a branched structure. The D-mannopyranose units in galactoglucomannan are, furthermore, known to be partly acetylated at the C-2 and C-3 positions. The degree of acetylation has been reported to be between 0.3 and 0.5 [27, 28]. In the early literature the existence of two types of galactoglucomannans was suggested [22]. The first type has been reported to be high in galactose with a typical galactose:glucose:mannose ratio of 1:1:3. In the second type, the galactose content is lower, and the mannose content higher (corresponding ratio 0.1:1:4). However, it has recently been suggested that these structures do not coexist in plants, but are rather the result of structural changes during extraction and isolation [12]. The average molecular mass of galactoglucomannan extracted with hot water from spruce wood has been reported to be in the range of 20 to 78 kDa [12, 28].

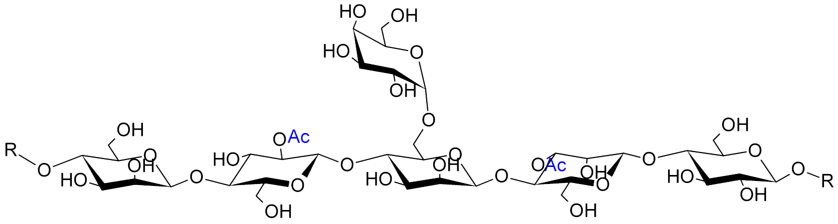

Figure 2.2: Molecular structure of galactoglucomannan.

Arabinoxylan

Arabinoxylan is the predominant hemicellulose in residues of agricultural crops such as wheat bran and barley husks. The molecular structure of arabinoxylan is shown in Figure 2.3. Arabinoxylans typically possess a β-1,4-linked D-xylopyranose backbone, which is substituted with 1,2- and/or 1,3-linked α-L-arabinofuranose residues. Furthermore, other side groups, e.g. D-glucopyranosyl uronic acid and its 4-O-methyl derivates, as well as ferulic acid, can be attached to a minor degree [29]. Native arabinoxylan is partly acetylated at some of the hydroxyl groups in the backbone. Similar to galactoglucomannan in spruce, these acetyl groups are easily cleaved under alkaline conditions [26]. The arabinose:xylose ratio in the macromolecule, and thus the degree of branching, can vary considerably in arabinoxylan originating from different species and parts of plants. In wheat bran the arabinose:xylose ratio has been reported to be about 1:1.07, while it is about 1:0.5 in wheat endosperm, and 1:0.78 in rye bran [29]. Furthermore, wheat bran arabinoxylan has been found to contain side chains comprising more than one arabinofuranose residue [29].

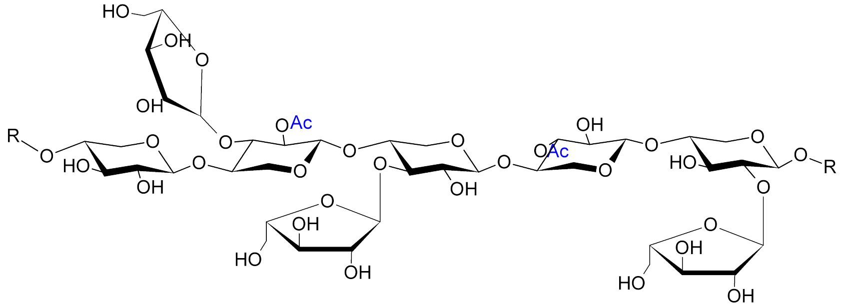

Figure 2.3: Molecular structure of arabinoxylan.

2.1.3 Lignin

Lignin is a complex macromolecule that provides plants with mechanical strength by “gluing” the other cell wall constituents together. In contrast to cellulose and hemicelluloses, lignin is not a polysaccharide, but is formed by polymerisation of the phenolic precursors coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. These monolignols have similar structures, but differ in the number of methoxy groups. During polymerisation the precursors are connected with each other in a random order resulting in a non-linear, highly cross-linked amorphous network of the phenylpropane subunits guaiacyl, syringyl and p-hydroxyphenyl (see Figure 2.4). The proportions of these subunits vary in the lignin of different plant species. In softwood, mainly guaiacyl units can be found, while hardwood lignin contains both guaiacyl and syringyl units, and all three units contribute to the final macromolecular structure in agricultural residues [22].

The dominating linkages within the lignin network are strong covalent bonds between carbon atoms and weak ether bonds. Furthermore, lignin forms ester and ether linkages with hemicelluloses and, to some extent, with cellulose. These linkages with the other biomass polymers can be cleaved by several methods (see extraction methods in Chapter 3). However, the use of these methods also leads to changes in the lignin structure, which means that it is almost impossible to isolate lignin in its native form. The structure illustrated in Figure 2.4 should therefore be regarded as one possible form of native lignin.

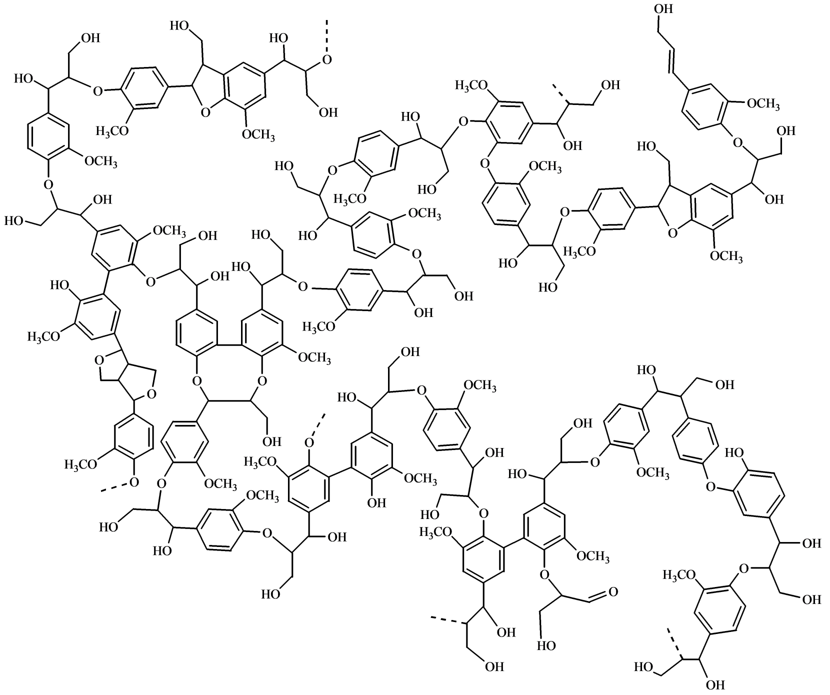

Figure 2.4: Molecular structure of softwood lignin. (Adopted from Ek et al. [30])

Investigations of the properties of various kinds of lignin have shown that lignin is a hydrophobic macromolecule, barely soluble in most solvents. The molecular mass of lignin isolated from softwood has been reported to be approximately 10 to 20 kDa [22, 31], and is thus lower than that of hemicelluloses and cellulose.

2.1.4 Residual components

Cellulose, hemicelluloses and lignin account for more than 90% of the dry matter in lignocellulose. The remaining 10% is made up of a large number of components such as extractives, pectins, proteins and inorganic substances. Extractives can especially be found in wood, where they make up about 1-2% of the total dry solids and about 20-40% of dry bark [22]. Extractives comprise a large group of low molecular mass substances, e.g. fatty acids, resin acids, triglycerides, sterols, stilbenes and tannins. Pectin compounds are polysaccharides that consist of D-galacturonic acid, D-galactose, L-arabinose and L-rhamnose residues, while proteins are polymeric substances that have amino acids as their monomeric units.

Chapter 3

Dissolution of biomass components in process streams

In the cell walls of plants cellulose, hemicelluloses and lignin are closely connected via covalent and non-covalent linkages. Ester and ether bonds cross-link, for example, lignin with hemicelluloses and cellulose [22]. Furthermore, hydrogen bonds are present between the hemicellulose and cellulose molecules [22]. The various linkages between the biomass components are generally rather stable, but they can be cleaved when biomass is treated with strong alkaline or acidic solutions and/or exposed to elevated temperatures and pressures. The rigid cell wall structure is disrupted as a consequence of such treatment, thereby solubilising biopolymers such as hemicelluloses and lignin. In the present chapter processes and methods that lead to the release and dissolution of biomass components in process streams are discussed. The composition and characteristics of the process streams used in the experimental studies of this work are also presented.

3.1 The pulping processes

The forestry industry is one of the largest consumers of lignocellulosic biomass as a feedstock for industrial products such as paper, cardboard and textiles. A large number of processes are involved, leading to different types of pulp and side streams containing various amounts of dissolved biomass components. The pulping processes can roughly be divided into chemical and mechanical methods. The most prevalent chemical methods are the sulphate process and the sulphite process. Mechanical methods can be classified into groundwood and refiner mechanical pulping.

3.1.1 Chemical pulping of wood

About 80% of the pulp produced from wood worldwide is chemical pulp, of which more than 90% is derived from the sulphate process. In this method the wood is first chipped and then cooked for several hours in a chemical solution containing sodium hydroxide (NaOH) and sodium sulphide. The temperature during cooking is about 160-180°C and the pressure about 7-11 bar. The high alkalinity and the elevated temperature and pressure result in considerable cleavage of the covalent bonds between cellulose fibres and the remaining biopolymers. The insoluble cellulose fibres are further processed after cooking to produce the chemical pulp. The residual biomass components, such as the hemicelluloses and lignin are, to a large extent, dissolved and removed in a side stream, called the black liquor.

The size distribution of the biomass components dissolved in the black liquor can be broad. On the one hand, large polymeric hemicellulose and lignin molecules can be found in this process stream as linkages in these macromolecules are quite stable under alkaline conditions. On the other hand, the high temperature and pH during sulphate pulping give rise to cleavage of the acetyl groups in hemicelluloses, and lead to some degradation of the carbohydrates. As a consequence of these reactions acetic acid, formic acid and hydroxylated carboxylic acids are formed, which together comprise about half of the organic substances in the black liquor [32]. Researchers have become increasingly interested in isolating the carboxylic acids from black liquor for non-fuel applications [32–34]. Furthermore, a method has been developed for the recovery of lignin (the LignoBoost process), which can be used as a solid fuel [35]. These recovery processes are not yet widely used in industry. However, a demonstration plant for the LignoBoost process has been in operation in Bäckhammar, Sweden, since 2007, with a production capacity of about 4000 tons of lignin per year [35]. Furthermore, Metso Corporation recently opened their first commercial LignoBoost plant in Plymouth, North Carolina [36].

3.1.2 Mechanical pulping of wood

Mechanical pulping processes are characterised by an extremely high yield, typically between 91 and 98% [37]. In contrast to chemical pulp, which is primarily composed of cellulose, pulp produced with mechanical methods consists of all the biomass components, including hemicelluloses and lignin. The presence of lignin reduces the brightness stability of the paper, which means that mechanical pulps are used primarily for the production of temporary paper such as newsprint and paperboard, and that used in catalogues and magazines [37]. In the groundwood process entire wood logs are ground by pressing them against the surface of a rotating grindstone. In the refiner mechanical process, wood chips are defibrated to produce mechanical pulp, usually in two consecutive refining stages. Prior to refining, the wood chips are often pretreated in order to soften the wood, thereby decreasing the energy required for processing. Thermal pretreatment with steam is, for example, used in thermomechanical pulp (TMP) mills, and a combination of thermal and chemical pretreatment, commonly with sodium sulphite, is applied in chemithermomechanical pulp (CTMP) mills. Figure 3.1 illustrates the various stages of a typical refiner mechanical pulping process using predominantly softwood, for example, spruce, as raw material.

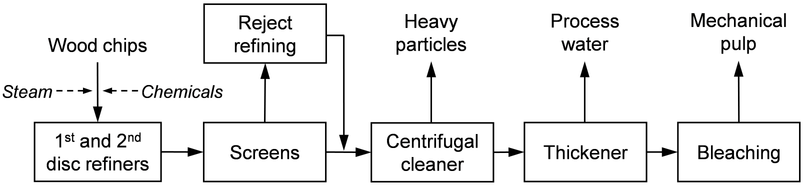

Figure 3.1: The process of refiner mechanical pulping. (Adapted from Sixta [38])

Dissolution during mechanical pulping

In mechanical pulp production the biomass is treated under milder conditions than in chemical pulping (lower pH, shorter treatment time), and thus the covalent linkages between the biomass components are cleaved to a lesser extent. As a consequence, non-cellulose biopolymers mostly remain attached to the cellulose fibres and contribute to the final mechanical pulp fraction. Some degree of dissolution of biomass components in the process water occurs during mechanical pulp production due to the elevated temperature and pressure during pretreatment and refining (115-155°C, 3-5 bar [37]), and the use of alkaline chemicals (e.g. sodium sulphite) in the CTMP process.

The dissolution of various wood components during mechanical pulping has been thoroughly investigated in a number of studies. About 10% of the hemicellulose galactoglucomannan and some of the arabinogalactan were found to be dissolved in the process water during thermomechanical pulping of Norway spruce (*Picea abies*) [39]. The amount of dissolved non-cellulose polysaccharides in softwood species other than spruce, as well as in hardwood species, has been found to vary between 1.5 and 7% [24, 25]. In softwood, mainly galactoglucomannan and pectins are dissolved [24], and in hardwood, glucuronoxylan and arabinogalactans are predominantly released into the process water [25].

The dissolution of various biomass components during thermomechanical and chemithermomechanical pulping has also been compared. The CTMP process results in a higher release of pectin, extractives and lignin, but a lower release of galactoglucomannan than the process of thermomechanical pulping [40]. Furthermore, the CTMP process leads to the release of substantial amounts of acetic acid and methanol as a consequence of the partial deacetylation and demethylation of galactoglucomannan and pectin [40, 41]. These findings are also in good agreement with those of Pranovich et al., who showed that the rate and the amount of spruce wood biopolymers that are dissolved in the water fraction increases with increasing alkalinity during extraction [42].

Quality of dissolved biomass components

While biomass components dissolved in process streams of chemical pulping are partly present in the form of degraded molecules, their native structure is mainly preserved after dissolution in the process water of mechanical pulp mills. The molecular mass of hemicelluloses extracted during thermomechanical pulping has been reported to be about 10 kDa [43], and the molecular mass of lignin about 1 kDa [43, 44]. It has also been found that hemicelluloses in TMP process water still carry their native acetyl groups [39], and that hemicelluloses in CTMP process water are at least partly acetylated [40–42]. The structural similarities between the hemicelluloses in the process water of mechanical pulp mills and native polysaccharides can be an advantage regarding their applicability for various high-value products, making their recovery interesting, in particular for operators of such pulp mills. Furthermore, energy can be generated in a chemical pulp mill from biomass components in the black liquor by burning them in the recovery boiler, while this is not possible in mechanical pulp mills. Instead, these substances are discharged with the wastewater, leading to higher demands on wastewater treatment and thus higher costs. For these reasons, experimental studies were carried out on process water from a TMP (Papers I and II) and a CTMP mill (Paper III).

3.2 Extraction from agricultural residues

In mechanical pulping, biomass components with relatively high molecular mass occur as a by-product dissolved in the process streams, from which they can be recovered. High molecular mass biomass components can also be prepared by extraction from plant material. This latter approach has the advantage that the properties of the extracted molecules can be controlled by tailoring the extraction procedure. Hemicelluloses have been extracted from the residues of a large number of annual crops including wheat [20, 45–47], barley [48–50], rice [51] and rye [52]. The extraction of hemicelluloses from various wood species has also been studied [10, 28, 48, 53]. However, the lower content and the different structure of lignin make extraction from agricultural residues less difficult [26]. Methods commonly applied for the extraction of hemicelluloses from agricultural residues are discussed below.

3.2.1 Alkali extraction

During alkali extraction hemicelluloses are liberated from the biomass structure using alkaline chemicals such as NaOH, calcium hydroxide ($Ca(OH)_2$), barium hydroxide ($Ba(OH)_2$) and potassium hydroxide (KOH). Alkaline treatment leads to cleavage of the ether and ester linkages between the various biomass components and dissolution of both water-soluble and water-insoluble hemicelluloses in the solvent. The molecular mass of the hemicelluloses in the extract can be rather high, which is regarded as a positive feature when using them in bio-based products. However, alkaline conditions can also lead to partial or even complete degradation of the polysaccharides (see Section 3.1.1). It is, for example, known that at a temperature of about 100°C a peeling reaction takes place, leading to the stepwise degradation of polysaccharides by removal of the reducing end group [2]. Furthermore, glycosidic linkages in the hemicellulose chain are cleaved at high pH when the temperature exceeds 150°C [2]. The removal of acetyl groups from hemicellulose molecules occurs at relatively mild alkaline conditions and temperatures (about pH 9 and 60°C) [42].

Several investigations have shown that high yields can be achieved during alkali extraction of high molecular mass hemicelluloses from agricultural residues. Typically, extraction temperatures below 100°C have been used in order to preserve the glycosidic bonds and avoid peeling reactions. $Ca(OH)_2$ and $Ba(OH)_2$ have been used to extract the hemicellulose glucuronoarabinoxylan from wheat bran [45]. At a high temperature of 95°C, about 50% of the arabinoxylans were extracted and were found to have a molecular mass as high as 400 kDa [45]. A yield of 57% was achieved during the extraction of arabinoxylan from barley husks at room temperature using NaOH and sodium chlorite for delignification [49]. The molecular mass of hemicelluloses in the extract was still about 35-45 kDa [49]. More than 90% of the original hemicelluloses can be extracted by the treatment of wheat straw with KOH and hydrogen peroxide at 50°C [46]. Considerable degradation of the polysaccharides has only been observed with long treatment times (16 h) and when using a high concentration of hydrogen peroxide (5%) [46].

Another feature of alkali extraction is the relatively high selectivity for the extraction of hemicelluloses from the biomass. A comparison of various extraction methods applied to wheat bran showed that the hemicellulose content in the dry matter of the extracts was markedly higher after alkali extraction than after alternative treatment such as steam explosion [47]. Thus, less undesired biomass components were co-extracted, which could facilitate the isolation and purification of hemicelluloses in the extract. However, the large amount of chemicals required is a disadvantage of this technique. One possible way to reduce this could be to recover the chemicals using nanofiltration. Alkaline extract from wheat bran was used as a hemicellulose source in some of the experimental studies included in this work (Papers IV and V), and the recovery of extraction chemicals was investigated in Paper VI.

3.2.2 Alternative extraction methods

Apart from alkali extraction, agricultural residues and wood have also been treated with microwaves [50], hot water [53], pressurised steam [47, 48, 54] and organic solvents [48] in order to extract hemicelluloses with high molecular mass. Extraction by microwave treatment is rather expensive, and thus probably not suitable for large-scale operation. Hot water treatment has the disadvantage that only water-soluble hemicelluloses will be released, leading to a relatively low yield. During steam explosion the biomass is exposed to pressurised steam at an elevated temperature (160-240°C) for a period of several seconds to a few minutes, followed by a sudden pressure release that disrupts the biomass structure and dissolves the hemicelluloses. Although high yields can be achieved with steam explosion [54], the method has been found to lead to more pronounced hemicellulose degradation, and thus lower molecular mass than alkaline extraction [47, 48]. The use of organic solvents, such as dimethyl sulphoxide, suffers from the disadvantage that the solvents are often expensive, hazardous to health and/or harmful to the environment. For further information on these alternative extraction methods the reader is referred to a recent review by Peng et al. [55].

3.3 Process streams used in this work

The experimental studies in this work were carried out with three different kinds of industrial process streams, all containing considerable amounts of dissolved biomass components. The first two streams were the process waters from a TMP mill and a CTMP mill. Both pulp mills used exclusively spruce wood as raw material for pulp production, and the biomass components dissolved in these streams thus originated from this type of softwood. The third process stream was the extract from an alkali extraction process using wheat bran as raw material and NaOH as extraction chemical. In the extraction process, the wheat bran was first washed and the starch was removed enzymatically prior to hemicellulose extraction.

The compositions of the three process streams are given in Table 3.1. The two pulp mill process waters had similar compositions and properties, but differed considerably from the alkaline extract. The two streams derived from spruce were rather diluted, with low total solids contents, while the alkaline extract contained substantial amounts of solid material. Due to the low concentration in the pulp mill process waters the density and viscosity of these streams were low and similar to those of water. The pH of the CTMP process water was almost neutral (pH 6.0) while the pH of the TMP process water was slightly acidic (pH 4.3). The dissolved hemicelluloses consisted mainly of mannose, glucose and galactose, indicating that galactoglucomannan is the major hemicellulose present in pulp mill process waters. It can be seen from Table 3.1 that the concentration of hemicelluloses was higher and the concentration of lignin lower in the TMP process water than in the CTMP process water. It is probable that the partial deacetylation of hemicelluloses and the sulphonation of lignin during chemithermomechanical pulping are responsible for the different amounts released into the process water. It is well known that both deacetylation and sulphonation affect the solubility of hemicelluloses and lignin [40]. Relatively high amounts of suspended solids were found in both pulp mill process streams. These substances consisted of, for example, fibre residues and wood extractives. The latter are known to form colloids that can be partly stabilised by galactoglucomannan [56].

In the alkaline extract from wheat bran, NaOH accounted for most of the total solids content, leading to a high pH (∼13.5). The concentration of hemicelluloses was considerably higher than in the other two process streams, and the hemicelluloses were found to be mainly arabinoxylan composed of arabinose and xylose units. As a consequence of the high concentration of hemicelluloses and other high molecular mass compounds, the viscosity of the alkaline extract was about 5 mPa s, measured at a temperature of 80°C and a shear rate of 100 s^{-1}. Thus, the viscosity of the wheat bran extract was about 14 times higher than the viscosity of water.

Table 3.1: Process streams used in this work.

	TMP process water	CTMP process water	Alkaline extract from wheat bran
Total Solids (g/l)	5.60±0.05	8.73±0.47	50.76±1.89
Susp. Solids (g/l)	1.16±0.50	3.25 [a]	—
Hemicelluloses (g/l)	1.30±0.07	1.17±0.24	7.93±0.32
Arabinose (g/l)	0.06±0.01	0.06±0.02	1.98±0.31
Galactose (g/l)	0.19±0.01	0.14±0.02	0.11±0.04
Glucose (g/l)	0.26±0.03	0.35±0.08	1.12±0.33
Xylose (g/l)	0.04±0.01	0.05±0.05	4.72±0.66
Mannose (g/l)	0.75±0.04	0.57±0.10	n.d.
Lignin (g/l)	0.84±0.05	1.13±0.17	—
Extractives (mg/l)	50.65±0.41	—	—
Ash (g/l)	1.96±0.20	1.56±0.20	31.02±1.45
NaOH (g/l)	—	—	40.01±1.87 [b]

[a] Based on a single measurement

[b] Based on the assumption that all ash consists of Na_2O

— Not analysed

n.d. Not detectable

Chapter 4

Unit operations for the separation of biomass components

In the previous chapter, industrial processes that result in process streams containing considerable amount of dissolved biomass components were discussed. In principle, these components can be used in a large variety of high-value applications, including hemicelluloses for barrier films in food packaging. However, process streams such as the process water from mechanical pulp mills and the alkaline extract from wheat bran have a complex composition, and apart the target biopolymers (in the present case hemicelluloses) also contain other substances such as extraction chemicals and co-extracted substances. As a consequence, processes are required with which the valuable hemicellulose molecules and residual substances in the mixture can be efficiently separated. In this chapter, various unit operations that could be suitable for this purpose are presented. The major focus is on the pressure-driven membrane filtration processes because of their extensive use in the present work.

4.1 Pressure-driven membrane filtration

Membrane filtration is a separation process that employs a semi-permeable membrane to separate two or more components from each other. In most cases this process uses a pressure difference between the two sides of the membrane as the driving force, and it is carried out in cross-flow mode, i.e. the feed stream flows tangentially over the membrane surface. Cross-flow operation has the advantage that it reduces the formation of a filter cake on the membrane surface, thereby allowing almost continuous operation. The feed stream is divided into a retentate and a permeate stream: the former containing all the substances that are retained by the membrane due to their large size or repulsive charge, and the latter composed of substances that are small enough to pass through the membrane pores.

Particles, macromolecules and ions can be separated using membrane filtration, making it suitable in a wide range of applications. Generally, microfiltration is used for the removal of particles and microorganisms, ultrafiltration is employed to remove macromolecules such as proteins and polysaccharides, nanofiltration can be used to remove monosaccharides, and reverse osmosis retains almost all kinds of molecules and ions apart from water. These pressure-driven membrane processes are gaining increasing popularity in industry because of their high selectivity, relatively low energy requirement and the possibility of using them in a wide temperature range without the need for the addition of chemicals.

4.1.1 Fundamental equations

The performance of a membrane filtration process is usually assessed in terms of the magnitude of the flux and the separation performance of the membrane. The flux is defined as the flow of permeate per unit area. It represents the capacity of the membrane process and determines the required size of the membrane plant. The ability of the process to separate components from each other can be assessed by comparing the retention of the individual components. In membrane processes the observed retention, R_{obs}, is distinguished from the true retention, R_{tr} [57]:

$$R_{obs} = 1 - \frac{C_p}{C_b} \tag{4.1}$$

$$R_{tr} = 1 - \frac{C_p}{C_m} \tag{4.2}$$

where C_p, C_b and C_m denote the concentration of the component in the permeate, the bulk solution and at the membrane surface, respectively. When a substance is retained to a certain extent by the membrane, a concentration gradient arises from the bulk solution to the membrane surface. This phenomenon, called concentration polarisation, is responsible for the fact that the observed retention is always lower than the true retention. In the present work, the observed retention was used, and is denoted R.

The flux through the membrane is mainly dependent on the properties of the feed solution and the operating conditions used during filtration. If the solution is pure water, the flux, J, can be expressed [57]:

$$J = \frac{\Delta P}{\eta_p \cdot R_m} \tag{4.3}$$

where ΔP is the transmembrane pressure, η_p is the dynamic viscosity of the permeate, and R_m is the membrane resistance. During the filtration of "real solutions" an osmotic pressure difference, $\Delta\pi$, can occur as a result of the difference in concentration at the membrane surface and in the permeate. This difference reduces the driving force for filtration and is particularly pronounced in membrane processes where the retained substances are small molecules or ions (for example, in reverse osmosis and nanofiltration). The flux can then be expressed by [57]:

$$J = \frac{\Delta P - \Delta\pi}{\eta_p \cdot R_m} \tag{4.4}$$

The formation of a cake or gel layer on the membrane surface is a common problem during microfiltration and ultrafiltration since substances in the feed stream of these processes are relatively large, which reduces back diffusion from the membrane surface. The presence of such a layer increases the resistance during filtration, and thus has a detrimental effect on the flux. In Eq. 4.5 this flux reduction is considered by an additional cake resistance, R_c, which is a function of the cake layer thickness and porosity [57]:

$$J = \frac{\Delta P}{\eta_p \cdot \left(R_m + R_c\right)} \tag{4.5}$$

The goal of many membrane filtration processes is to concentrate and/or purify a certain component in a feed stream. This goal can be achieved by selecting a membrane that retains the substance of interest, but is permeable to the impurities. The target component can be concentrated by continuously bleeding off the permeate from the membrane process and recirculating the retentate stream. In batch mode, assuming the retention to be constant, the concentration of the desired product in the retentate stream can be determined from the initial concentration in the feed, C_0, the observed retention of the substance, and the volume reduction, VR [57]:

$$C_r = C_0 \cdot \left(\frac{1}{1-VR}\right)^R \tag{4.6}$$

where the volume reduction is defined as the ratio of the permeate volume, V_p, to the initial feed volume, V_0 [57]:

$$VR = \frac{V_p}{V_0} \tag{4.7}$$

The film model can be used to derive the relation between the flux and the concentration of the solute by creating a mass balance over the boundary layer at the membrane surface [57]:

$$J = k \cdot \ln\left(\frac{C_m - C_p}{C_b - C_p}\right) \tag{4.8}$$

According to this model, a plot of the flux against the logarithm of the concentration of the solute in the feed gives a straight line, which intersects the x-axis at the maximal concentration achievable with the membrane process. The mass transfer coefficient, k, is assumed to be constant and can be determined from the slope of this straight line.

Running filtration to a high volume reduction allows a high concentration of the desired substance to be achieved in the final retentate stream, as can be seen from Eq. 4.6. However, a high concentration is obtained at the expense of the yield when the product is not completely retained by the membrane. With increasing volume reduction the yield, Y, (or recovery) decreases in a membrane concentration process according to [57]:

$$Y = \frac{(1-VR) \cdot C_r}{C_0} = (1-VR)^{(1-R)} \tag{4.9}$$

It should be pointed out that Eq. 4.9 is valid in this form only for products recovered in the retentate. When the product is recovered in the permeate, a low retention is desired, and the highest yield is also achieved by running filtration to a high volume reduction.

4.1.2 Flux-enhancing methods

Low flux is one of the major problems experienced during pressure-driven membrane filtration. One way of increasing the flux is to increase the transmembrane pressure, i.e. the force driving filtration. However, this increases the transport of retained substances to the membrane surface, which can lead to the formation of a cake or gel layer. When such a layer is formed, the flux will level off and reach a limiting value, completely independent of pressure. During micro- and ultrafiltration of complex process streams the levelling-off of the flux can occur at low transmembrane pressure, and the limiting flux can be too low for economically feasible operation. Furthermore, the separation performance during filtration can be impaired by the cake/gel layer. In such cases, flux-enhancing techniques that counteract the formation of a layer of deposited material can be beneficial.

Most flux-enhancing methods are based on increasing the turbulence at the membrane surface, for example, increasing the cross-flow velocity, the use of helical baffles, rotational or vibrating membrane modules [58], and the application of backflushing or backpulsing. Backpulsing was used during the microfiltration of TMP process water, described in Paper II. During backpulsing, the permeate flow through the membrane is reversed, usually for less than a second, at regular intervals. The reversed permeate flow removes material deposited on the membrane surface, which can then be carried away by the cross-flow. Backpulsing has been shown to be beneficial in various applications, for example, the microfiltration of milk [59], beer [60], oil-water suspensions [61, 62], yeast suspensions [62, 63], and protein-containing mixtures [64]. However, the technique can only be used with membranes and modules that can withstand such pressure fluctuations, i.e. mainly ceramic membranes.

4.1.3 Separation of biomass components with membranes

The membrane filtration processes used in the experimental studies in this work were microfiltration, ultrafiltration and nanofiltration. These processes were applied to recover valuable biomass components, in particular hemicelluloses, from the process streams described in Section 3.3. Microfiltration was primarily used to remove suspended matter and colloids, ultrafiltration was applied for hemicellulose recovery, and nanofiltration was used to obtain a concentrated lignin fraction and a permeate pure enough for reuse (e.g. pure water or a solution of the extraction chemical). Other researchers have applied membrane filtration processes for similar purposes on a large number of biomass-containing process streams, including black liquor [65–67], mechanical pulp mill process water [43, 68–70], wood hydrolysate [71–74] and solutions obtained after extraction from agricultural residues [17, 75, 76]. In most cases the primary goal was to recover either hemicelluloses or lignin from the process streams.

Recovery of hemicelluloses

Interest in utilising hemicelluloses for high-value products has evolved quite recently. As a consequence, much research has been undertaken on methods of recovering these substances from various process streams and waste materials. In this context, membrane filtration processes are often used to separate hemicelluloses from other biomass components and impurities.

One of the first investigations on the recovery of hemicelluloses in the process water from the pulp and paper industry was carried out by Willför et al. [70, 77]. In their study a method was developed with which hemicelluloses were first separated from lipophilic extractives and dissolved aromatic compounds (lignans and lignin) using flocculation and adsorption. Ultrafiltration was then applied to further purify and concentrate the hemicelluloses. It was reported that hemicelluloses with high purity could be produced at a yield of about 5 kg per ton of pulp with this method. Persson et al. used similar pulp mill process streams as a source of hemicellulose, but investigated the performance of membrane filtration in more detail [43, 78]. The economic feasibility of a large-scale recovery process has also been evaluated [69]. The method used consisted of microfiltration to remove undissolved compounds, followed by ultrafiltration to separate the hemicelluloses from lignin. Diafiltration was suggested to further increase the purity of the final hemicellulose fraction [68, 69]. During the ultrafiltration of pulp mill process water it was found that hydrophilic membranes were more suitable than hydrophobic membranes, as they became less fouled by organic substances [78]. Furthermore, a membrane cut-off of 5 to 10 kDa was reported to be optimal with respect to flux and the separation of hemicelluloses from lignin [43]. A high retention of hemicelluloses (above 90%), a relatively low retention of lignin (30-50%), and a high flux (up to 190 l/m^2h) were achieved with the hydrophilised polysulphone membrane UFX5pHt from Alfa Laval Nakskov A/S (cut-off 5 kDa), which was also the membrane of choice in the ultrafiltration experiments described in Papers I and III.

Considerable effort has also been devoted to concentrating and purifying hemicelluloses after hot water extraction of wood. Al Manasrah et al. [73] studied the performance of various regenerated cellulose membranes (cut-off 5, 10 and 30 kDa) during the recovery of galactoglucomannan from spruce hydrolysate. With the most open membrane, an unacceptably low retention of hemicelluloses was obtained, while good separation between hemicelluloses and lignin was observed with the most dense membrane. They concluded that a membrane cut-off of around 5 kDa was best for hemicellulose recovery, in line with the results presented by Persson et al. [43]. The purification of concentrated hemicelluloses by diafiltration was subsequently investigated [73], but no increase in hemicellulose purity was observed due to the similar retention of hemicelluloses and lignin. This finding is in contrast to an earlier study, where hemicellulose purity was increased from 57 to 77% by diafiltration with a 1 kDa membrane [68]. Other researchers have reported higher hemicellulose purities using other techniques such as ethanol precipitation and size-exclusion chromatography [68, 70, 74].

Apart from the investigation by Al Manasrah et al. [73], other research on wood hydrolysate has been carried out to fractionate hemicelluloses in well defined size fractions using membrane filtration. González-Munõz et al. [71] and Song et al. [74] employed a series of consecutive ultrafiltration steps using decreasing membrane pore size from the first to the last step of the process. The results of these investigations showed that hemicelluloses differing in molecular mass could be separated into various fractions using such an ultrafiltration cascade. Furthermore, lignin and monosaccharides were mainly found in the low molecular mass fraction, showing that purified hemicelluloses with high molecular mass can be obtained with this procedure.

Solutions obtained after extraction from agricultural residues represent the third group of process streams from which hemicelluloses have been recovered by membrane technology. In this kind of process stream hemicelluloses must not only be separated from other biomass components, but often also from the chemicals used for extraction. As the pH of the extracts can be rather high, the use of ceramic membranes is not uncommon. Ultrafiltration has been used to recover hemicelluloses extracted from barley husks [48, 75], wheat bran [17, 19, 20, 79], rice husks [76, 80] and corn stalks [81]. A detailed investigation of membrane filtration of an extraction solution, in which the performance of several ultra- and nanofiltration membranes was evaluated, was carried out by Vegas et al. [76]. The results clearly showed that, by using an appropriate membrane, monosaccharides and non-saccharides could be efficiently removed from oligomeric hemicelluloses intended for use in health food applications. In two other investigations it was shown that polymeric arabinoxylans could be recovered from wheat bran using ultrafiltration on a pilot scale [20, 79]. Papers IV and V present detailed investigations of the performance of ultrafiltration of an alkaline extract from wheat bran.

One of the major challenges identified during membrane filtration of process streams containing hemicelluloses is the reduction in membrane capacity as a result of fouling. In a recent investigation, Puro et al. [82, 83] showed that especially lipophilic wood extractives present in such process streams can cause severe fouling of ultrafiltration membranes. A promising way to improve membrane performance could, therefore, be to remove or degrade foulants prior to membrane filtration. Koivula et al. [72] and Hasan et al. [84] studied various methods of pretreatment (e.g. activated carbon adsorption, pH adjustment, oxidation by pulsed corona discharge, microfiltration) on different wood hydrolysates, and also investigated the influence on subsequent membrane filtration. Persson et al. [78] carried out a similar investigation on pulp and paper wastewater. The results of these investigations revealed that fouling could be reduced, and the membrane flux substantially increased by appropriate pretreatment of the process streams. However, it was also pointed out that the method of pretreatment must be chosen carefully, as in some cases poorer membrane performance was observed [72]. Various methods of pretreatment were also studied in this work; the effect of pre-filtration on subsequent hemicellulose recovery by ultrafiltration is presented in Paper V.

Recovery of lignin

One of the most suitable process streams for lignin recovery is the black liquor from the sulphate pulping process (see Section 3.1.1). Lignin is one of the major components in this kind of process stream (concentration above 50 g/l), but its recovery requires separation from the cooking chemicals used in the pulp mill. One method that can be used for this purpose is the precipitation of lignin at reduced pH, which is the concept on which the LignoBoost process is based. After precipitation (e.g. with carbon dioxide), solid lignin can be filtered in a filter press and the filter cake redispersed for further purification of the lignin fraction [35]. An alternative to this is membrane filtration. Lignin can be concentrated in the retentate using ultrafiltration, while the cooking chemicals pass through the membrane pores. Wallberg showed that a lignin concentration of 155-240 g/l and a purity of 58-78% could be achieved using tubular ceramic membranes with a cut-off ranging from 5 to 15 kDa [67]. The additional use of diafiltration or precipitation may be of interest if an even higher purity or a solid lignin fraction is required.

The hemicelluloses dissolved in black liquor can cause some problems during the recovery of lignin. When precipitation is used, hemicellulose molecules can co-precipitate [66], reducing the purity of the lignin fraction, and increasing the specific filtration resistance during subsequent filtration in a filter press [85]. These problems can be reduced by separating lignin and hemicelluloses prior to precipitation. Jönsson et al. [65] showed that most hemicelluloses could be retained by a 15 kDa ultrafiltration membrane under appropriate conditions, while most of the lignin was recovered in the permeate. The lignin in the permeate can subsequently be concentrated by nanofiltration before the LignoBoost process is applied for recovery. A recent study by Wallmo et al. [85] revealed that the removal of hemicelluloses in this way had positive effects on the filterability in the filter press used after lignin precipitation. These investigations and other state-of-the-art research on lignin recovery with membranes were recently summarised in a review by He et al. [86].

All the studies on hemicellulose and lignin recovery described above illustrate the potential of membrane filtration for the separation of biomass components in complex mixtures. However, it was also shown that membrane processes must be tailored to the specific process solution in order to reduce fouling, and in some cases additional unit operations were required to achieve the best membrane performance.

4.2 Conventional dead-end filtration

Conventional dead-end filtration in filter presses, rotary-drum filters, belt filters and disc filters is an alternative mode to cross-flow filtration, and is frequently used in industry to remove large particles (typical size 1 μm up to several mm) from a process stream. Common applications are, for example, the clarification of beverages (beer, juice), the treatment of water and wastewater, and the dewatering of pulp after chemical or mechanical pulping of wood. In this technique the feed stream is directed vertically onto the filter medium instead of tangentially, as is the case during cross-flow filtration. Large components in the feed solution are retained, and form a filter cake on top of the filter medium. This filter cake increases rapidly in thickness with the amount of feed solution that is processed. As a consequence, the filter cake resistance exceeds the resistance of the filter medium, R_m, during dead-end filtration after only a short time, and thus governs the filtration performance, i.e. the filtration capacity and filtrate purity.

A common way of evaluating a constant-pressure filtration process, carried out in dead-end mode, is to plot the ratio of filtration time and filtrate volume, t/V, against the filtrate volume, V, according to [87]:

$$\frac{t}{V} = \frac{\alpha\kappa\eta}{2A^2\Delta P} \cdot V + \frac{R_m\eta}{A\Delta P} \tag{4.10}$$

where α is the specific filter cake resistance, κ is a concentration parameter, η the dynamic viscosity of the filtrate, A the filtration area and ΔP the pressure difference between the two sides of the filter medium. Such a plot often gives a straight line, and α and R_m can be determined from the slope and the intercept, respectively. When a solution is difficult to filter (i.e. $\alpha > 10^{12}$ m/kg), it is common to pre-coat the filter medium with a filter aid such as kieselguhr, or to mix the filter aid into the solution prior to filtration. This leads to the formation of a less compact filter cake, which often improves the filtration performance.

Dead-end filtration is generally not suitable for the separation of biomass components as the technique is too coarse to separate dissolved macromolecules. However, the process can be used cost-efficiently, for example, for lignin recovery in the LignoBoost process, where lignin is first precipitated [85]. Furthermore, it can provide an effective means of protecting membranes from feed channel blocking or improving the performance in a subsequent membrane filtration stage. No detailed studies were carried out on dead-end filtration in the present work, but the technique was used for improvement of membrane filtration, with either a filter press (Paper V) or a rotary-drum filter (Papers I and II), depending on the process solution investigated.

4.3 Non-filtration methods

The separation of biomass components using the filtration processes discussed above is mainly achieved as a consequence of size differences. Other molecular properties that can also be exploited are the solubility of biomass components in certain solvents, as well as their surface charge. Methods such as precipitation, extraction and adsorptive chromatography (e.g. ion-exchange chromatography) provide separation based on differences in these properties. Generally, such non-filtration methods are more costly than filtration as a result of either the large amount of chemicals required or the relatively low capacity. However, in order to achieve a high purity and thus a high value of the final product non-filtration methods may be of interest, for example, in combination with filtration.

There are several examples of the use of non-filtration methods to separate biomass components from each other in order to produce a purified hemicellulose fraction. For example, colloidal wood extractives can be flocculated and subsequently easily removed from dissolved hemicelluloses by the addition of a starch-based cationic polymer to pulp mill process water [70]. Adsorptive chromatography with a hydrophobic ion-exchange resin has been applied in various studies for the removal of aromatic compounds, in particular lignans and lignin, from hemicellulose-containing solutions [17, 44, 70, 80, 88], and the precipitation of hemicelluloses in organic solvents such as ethanol, methanol and acetone has been shown to be suitable for the final purification of the product molecules. Good results regarding the purity and yield of hemicelluloses have been achieved with precipitation, which explains the extensive use of ethanol precipitation [17, 47, 48, 70, 74, 80, 81, 89]. By varying the amount of solvent applied, precipitation can be used to fractionate hemicelluloses into various size fractions as an alternative to membrane-based fractionation processes [74, 89]. A comprehensive review has recently been published in which the most common non-filtration methods applied for purification and fractionation of hemicelluloses are presented and discussed [55].

Chapter 5

Separation of components in pulp mill process water

In the present work, the separation of hemicelluloses from residual components in pulp mill process water was studied with two different process configurations, as schematically illustrated in Figure 5.1. Larger particles, suspended matter and colloids were removed from the process water by pre-filtration and microfiltration, and hemicelluloses and lignin were then separated in a third stage by ultrafiltration, in both configurations. In Configuration I, a concentrated, purified hemicellulose fraction was recovered in the ultrafiltration retentate, and the ultrafiltration permeate was further treated by nanofiltration in order to produce a pure water stream. In Configuration II, the hemicelluloses in the ultrafiltration retentate were enzymatically cross-linked, thereby increasing their molecular mass. The hemicelluloses were subsequently fractionated into two product streams in a second ultrafiltration stage. Hemicelluloses with high molecular mass were accumulated in the retentate, while those with low molecular mass were withdrawn with the permeate.

The initial work was carried out using process water from a TMP mill ([43, 69], Papers I and II). Configuration I was followed with this stream, and the performance of each stage of the process was studied. In a continuation of these studies, it was investigated whether a similar process configuration would also be suitable for process water from a CTMP mill (Paper III). However, Configuration II was used with this second process stream to study the possibility of recovering hemicelluloses with particularly high molecular mass.

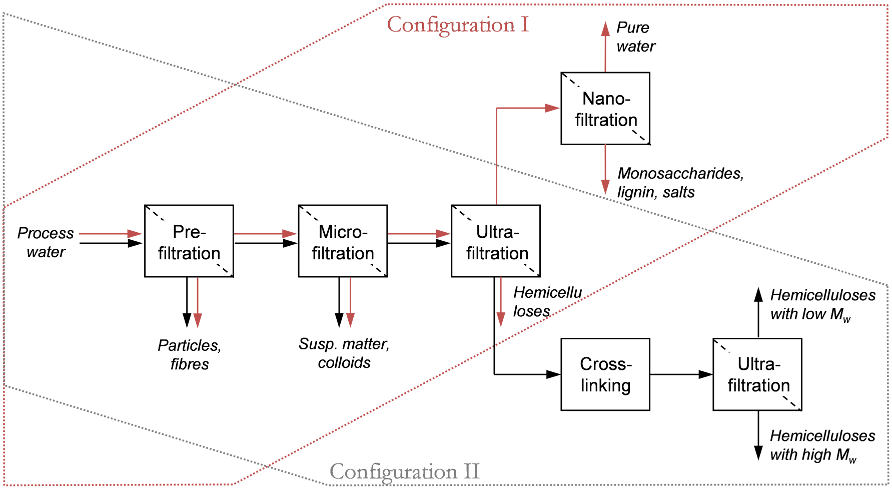

Figure 5.1: Schematic illustration of the two process configurations used to fractionate biomass components in pulp mill process water. Configuration I was applied to process water from a TMP mill, while Configuration II was applied to CTMP process water. (M_w denotes molecular mass).

This chapter focuses on the findings obtained during the development of the two process configurations, based on the results given in Papers I, II and III. The aim of these investigations was to evaluate and improve the performance of all stages in the processes, so that the highest possible hemicellulose yield and purity, and the lowest possible process cost could be achieved.

5.1 Removal of suspended matter and colloids

The concentration of suspended matter in the process water from the TMP and CTMP mill was about 1.2 and 3.3 g/l, respectively (see Table 3.1). Furthermore, wood extractives were dispersed in the process streams forming colloids. Before hemicelluloses are concentrated by ultrafiltration, these substances must be removed to the highest possible degree, for two reasons. Firstly, dispersed substances would lead to a reduction in hemicellulose purity in the ultrafiltration retentate, and secondly, they could impair ultrafiltration by blocking the flow channels of the membranes. Microfiltration was the method mainly applied for complete removal of suspended matter and colloids from TMP and CTMP process water (Papers I-III), however, conventional dead-end filtration was also investigated as an alternative.

5.1.1 Microfiltration versus dead-end filtration

The application of conventional dead-end filtration for particle removal has the general advantage of being less costly than microfiltration. However, as the pore size of a dead-end filter cloth is relatively large, it cannot be guaranteed that suspended matter and colloids will be removed to a sufficient degree. The efficiency of both techniques was therefore investigated in a comparative study on CTMP process water (unpublished data). Dead-end filtration was carried out in a rotary-drum filter and in a filter press using the same 10 μm filter cloth (the equipment is described in Papers I and V). In the filter press, kieselguhr was used as a filter aid (concentration 0.5 wt%). The pore size of the membrane used for microfiltration was 0.2 μm (additional information on the membrane is given in Papers I and II).

As can be seen from Table 5.1, the turbidity of the filtrates after dead-end filtration was still relatively high, indicating the presence of residual dispersed substances. In the microfiltration permeate the turbidity was, however, considerably reduced. Microfiltration is therefore necessary in the processes illustrated in Figure 5.1, especially when a hemicellulose fraction with high purity is required. Conventional dead-end filtration could, however, be used to remove the largest particles in order to protect the microfiltration membranes.

Table 5.1: Efficiency of various methods for the removal of suspended matter and colloids from pulp mill process water.

	Turbidity (NTU)	Total solids (g/l)	Hemicellul. (g/l)	Lignin (g/l)
CTMP process water	8440	9.31	1.30	0.98
After drum filtration	3915	6.82	1.25	0.95
After pressure filtration	696	5.67	1.26	0.92
After microfiltration	5	4.19	0.78	0.77

(NTU denotes nephelometric turbidity unit)

As can be seen from Table 5.1, microfiltration removed not only suspended matter and colloids, but also reduced the amount of hemicelluloses in the process water. This reduction in hemicellulose concentration is obviously undesirable, as it decreases the amount of hemicelluloses that can be recovered in the purified fraction from the ultrafiltration stages of the process. A primary goal of this work was therefore, not only to achieve a high flux during microfiltration, but also to investigate the possibility of reducing the hemicellulose loss, for example, by varying the membrane pore size and operating conditions. Some of these investigations were carried out with process water from the TMP mill, in which high losses of hemicelluloses were also observed.

5.1.2 Influence of pore size

The performance of three tubular ceramic membranes was investigated during microfiltration of TMP process water (Paper II). The membranes were made of the same material (α-aluminium oxide), and were all manufactured by Atech Innovations GmbH. The membrane pore sizes were 0.2, 0.4 and 0.8 μm.

All the membranes investigated efficiently removed suspended matter and colloids from the process water. However, a considerable difference in performance was observed regarding membrane flux and the retention of macromolecules. The retention of hemicelluloses and lignin was lowest with the most open membrane (0.8 μm) (see Table 5.2), and increased with decreasing pore size. Thus, from a separation point of view, the 0.8 μm membrane would be most favourable, as more hemicelluloses could be recovered in the microfiltration permeate than with the denser membranes. However, this membrane suffered from low flux.

Table 5.2: Influence of pore size on macromolecule retention during microfiltration of TMP process water (Paper II).

	0.2 μm	0.4 μm	0.8 μm
Retention of hemicelluloses (%)	51	35	28
Retention of lignin (%)	14	15	11

The flux of the membranes is illustrated as a function of filtration time in Figure 5.2. A considerable decrease in flux was seen with the 0.8 μm membrane, a moderate decrease with the 0.4 μm membrane, and almost no decrease with the membrane with the smallest pores (0.2 μm). The flux decline seen with the more open membranes is probably the result of suspended matter blocking the entrance of the membrane pores. This phenomenon has been observed previously, for example, during the microfiltration of wood hydrolysate [84]. Such blockage of the membrane pores probably does not occur in the 0.2 μm membrane due to the small pore size compared with the size of the suspended matter. Liu et al. [90] also reported increasing flux with decreasing pore size during the microfiltration of black liquor.

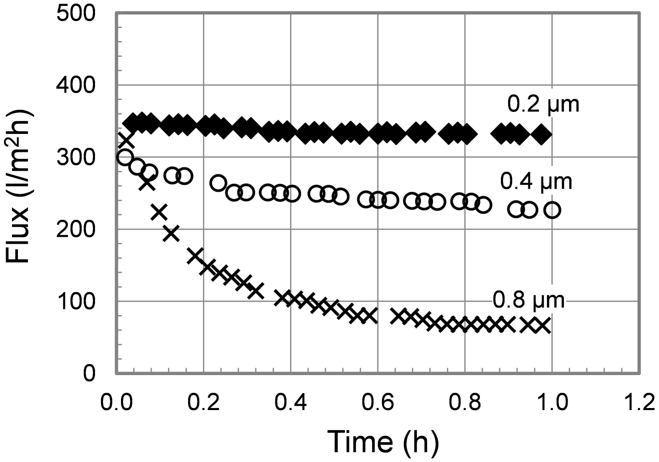

Figure 5.2: Influence of pore size on flux during the microfiltration of TMP process water (Paper II). The cross-flow velocity was 4 m/s, the transmembrane pressure 0.5 bar, and the temperature of the process water 80°C.

As well as showing a decline in flux during filtration, the pure water flux could not be recovered by chemical cleaning of the 0.4 and 0.8 μm membranes. Such irreversible fouling after a short filtration time would be unacceptable in a large-scale plant, where membranes must provide sufficient flux over several months, or even years. For this reason, only the 0.2 μm membrane can be used in this application, despite the fact that it retains a greater proportion of the hemicelluloses.

5.1.3 Influence of operating conditions

The influence of operating conditions on flux and retention during microfiltration of both types of pulp mill process water (TMP and CTMP) was investigated using the 0.2 μm membrane (Paper II and unpublished data). The experiments on TMP process water were carried out at 80°C, while during the microfiltration of CTMP process water the temperature was reduced to 60°C. Eighty degrees is the temperature of the process water at the TMP mill, and 60°C is a tolerable temperature for technical laccase enzymes that could be used in the cross-linking stage of Configuration II (Petri Oinonen, private communication).

A high flux was achieved at the higher cross-flow velocity (5 m/s) during microfiltration of both pulp mill process streams, as shown in Figure 5.3. Furthermore, the flux increased markedly with increasing transmembrane pressure at this high cross-flow velocity. The flux increase was less pronounced at the lower cross-flow velocity of 3 m/s, at which the flux levelled-off above 0.5 bar as a result of cake layer formation, and reached its limiting value at a transmembrane pressure of 0.7 bar. Low cross-flow velocity in combination with elevated transmembrane pressure is therefore not recommended during the microfiltration of either of these two process streams. The flux obtained in the present work was of the same magnitude as that obtained during the microfiltration of a similar process stream (wood hydrolysate) by other researchers [84].

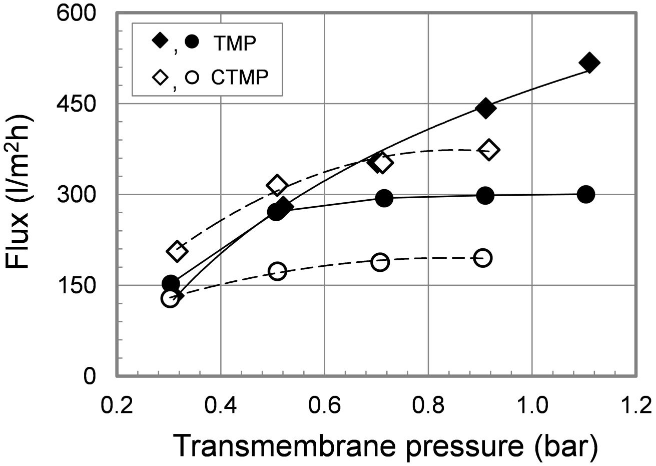

Figure 5.3: Influence of operating conditions on flux during the microfiltration of TMP and CTMP process water (Paper II and unpublished results). Diamonds: cross-flow velocity 5 m/s. Circles: cross-flow velocity 3 m/s. The temperatures of the TMP process water and CTMP process water were 80°C and 60°C, respectively.

Single hemicellulose and lignin molecules are much smaller than the pore size of a 0.2 μm membrane. Therefore, macromolecule retention during microfiltration of the two pulp mill process streams should be relatively low. However, as can be seen in Figure 5.4, the hemicellulose retention was $\sim$33% during microfiltration of CTMP process water and as high as $\sim$66% during microfiltration of process water from the TMP mill. The retention of lignin was $\sim$18% for CTMP process water and $\sim$9% for TMP process water. The retention of both macromolecules was found to be almost independent of the operating conditions, apart from a slight decrease in hemicellulose retention with increasing cross-flow velocity during the microfiltration of CTMP process water.

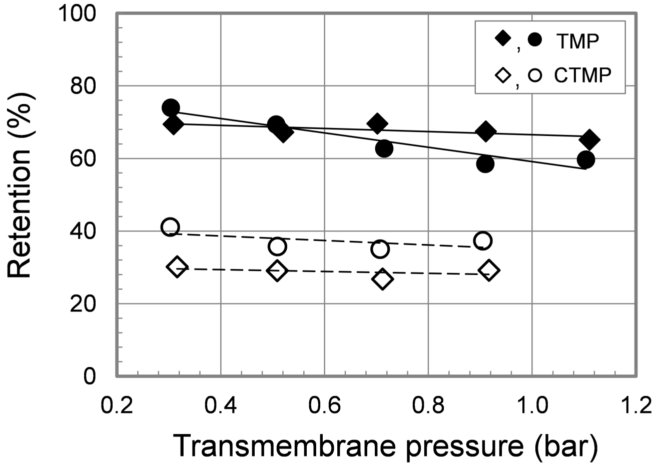

Figure 5.4: Influence of operating conditions on hemicellulose retention during microfiltration of TMP and CTMP process water (Paper II and unpublished results). Diamonds: cross-flow velocity 5 m/s. Circles: cross-flow velocity 3 m/s. The temperatures of the TMP process water and CTMP process water were 80°C and 60°C, respectively.

The formation of a cake/gel layer on the membrane surface has been suggested as a possible explanation of the increase in hemicellulose (27-78%) and lignin (52-53%) retention during microfiltration of wood hydrolysate [84]. However, this cannot be the only cause of the high retention seen in the present work. In Figure 5.3 it can be seen that at a cross-flow velocity of 5 m/s the flux increases with increasing transmembrane pressure for TMP process water, indicating the absence of a cake layer on the membrane surface. However, hemicellulose retention was as high as under operating conditions where cake layer formation occurred. Therefore, other phenomena apart from cake layer formation must be involved in the increase in retention. The ability of hemicelluloses to form aggregates in aqueous solutions has been demonstrated [91], and it was also found that hemicelluloses can adsorb onto cellulose surfaces and stabilise colloidal wood extractives [11, 12, 56, 92, 93]. Thus, aggregation and adsorption could be possible explanations of the high retention seen during the microfiltration of TMP and CTMP process water.

5.1.4 Achievable yield and flux during concentration

In order to recover as much of the hemicelluloses as possible in the microfiltration permeate, it is of the utmost importance that microfiltration is run to a high volume reduction. The performance of the 0.2 μm membrane was investigated during the concentration of TMP and CTMP process water under constant operating conditions (Papers I and III). In these experiments the retentate was recirculated to the feed tank, while the permeate was continuously withdrawn from the system.

In Figure 5.5 it can be seen that most of the hemicelluloses in TMP and CTMP process water could be recovered in the permeate, despite the fact that the hemicellulose retention during microfiltration was 57-88% and 30-77% for TMP and CTMP process water, respectively. These high yields were achieved because microfiltration could be continued to a volume reduction of 98%. Although marked differences in retention were observed, the yields obtained for both process streams were very similar. This shows that high volume reduction is actually more important than low hemicellulose retention in obtaining a high yield using microfiltration.

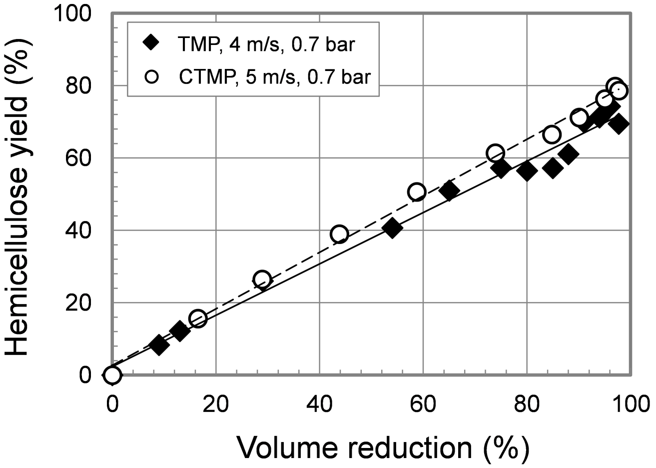

Figure 5.5: Increase in hemicellulose yield during the concentration of TMP and CTMP process water by microfiltration (data from Papers I and III). The temperatures of the TMP and CTMP process water were 80°C and 60°C, respectively.

The flux during the concentration of the process streams is illustrated in Figure 5.6. For both types of process water a high initial flux was observed, which was maintained until a volume reduction of 80% was reached. At higher volume reductions, the flux declined steeply, which is probably the result of the considerable increase in the concentration of suspended matter in the feed tank. The average flux during concentration to a volume reduction of 98% was 300 l/m^{2}h for TMP process water; somewhat higher than during the concentration of CTMP process water (260 l/m^{2}h). This higher flux could be explained by the higher temperature during the experiments with TMP process water and the lower initial concentration of suspended matter and colloidal extractives in this process stream.

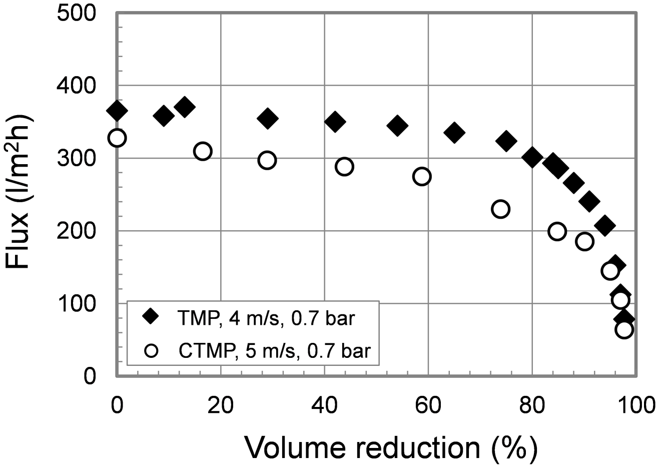

Figure 5.6: Flux during the concentration of TMP and CTMP process water by microfiltration (Papers I and III). The temperatures of the TMP process water and CTMP process water were 80°C and 60°C, respectively.

Both high flux and high hemicellulose yield are desirable during microfiltration, since both result in a decrease in the process cost. However, increasing volume reduction has opposite effects on the flux and yield, as can be seen in Figures 5.5 and 5.6. The value of volume reduction that leads to the most cost-efficient microfiltration process can be determined, but this requires knowledge concerning the membrane equipment and operating cost, as well as the future market price of hemicelluloses.

5.1.5 Flux enhancement by backpulsing

Backpulsing may allow microfiltration to be operated at lower cross-flow velocities, without incurring any significant flux decline. Lower cross-flow velocities require less energy for circulation, thus reducing the operating cost of a large-scale plant. Furthermore, if hemicellulose retention is partly due to cake layer formation, dispersing the cake layer by backpulsing would reduce the hemicellulose loss. The influence of backpulsing on flux and retention was therefore studied at two cross-flow velocities at constant transmembrane pressure, using TMP process water as the feed solution (Paper II). The duration of the pulse (pulse length) and the interval between the pulses (forward filtration time) were varied.

When microfiltration was operated under conditions where no cake formation occurs, i.e. a high cross-flow velocity of 5 m/s, backpulsing obviously did not increase the flux. However, at the lower cross-flow velocity (3 m/s), the technique was found to have a marked flux-increasing effect, indicating that cake layers of suspended matter could be efficiently removed from the membrane surface. In Figure 5.7 it can be seen that the greatest flux improvement occurred with the shortest pulse length (0.25 s) and the longest forward filtration time (5 s), i.e. backpulsing conditions under which the duration of reverse flow was at a minimum. Under these conditions, the application of backpulsing increased the flux from 300 to 420 l/m^2h. At a cross-flow velocity of 5 m/s, the flux was 480 l/m^2h without backpulsing. Thus, the flux obtained when operating microfiltration at the lower cross-flow velocity of 3 m/s can be increased to almost the value at the higher cross-flow velocity of 5 m/s by the application of backpulsing. It should be noted, however, that the backpulsing parameters were not optimized, and that a greater improvement in flux may be possible by running at a forward filtration time longer than 5 s, as indicated by results shown in Figure 5.7.

Backpulsing was not successful in significantly reducing the retention of hemicelluloses during microfiltration. Retention was more or less unaffected at the higher cross-flow velocity, and decreased from 59% to 50% at the lower cross-flow velocity. This finding confirms the hypothesis that although cake layer formation may contribute to macromolecule retention, other mechanisms (e.g. aggregation and adsorption) have a greater impact on hemicellulose retention during the microfiltration of pulp mill process water.

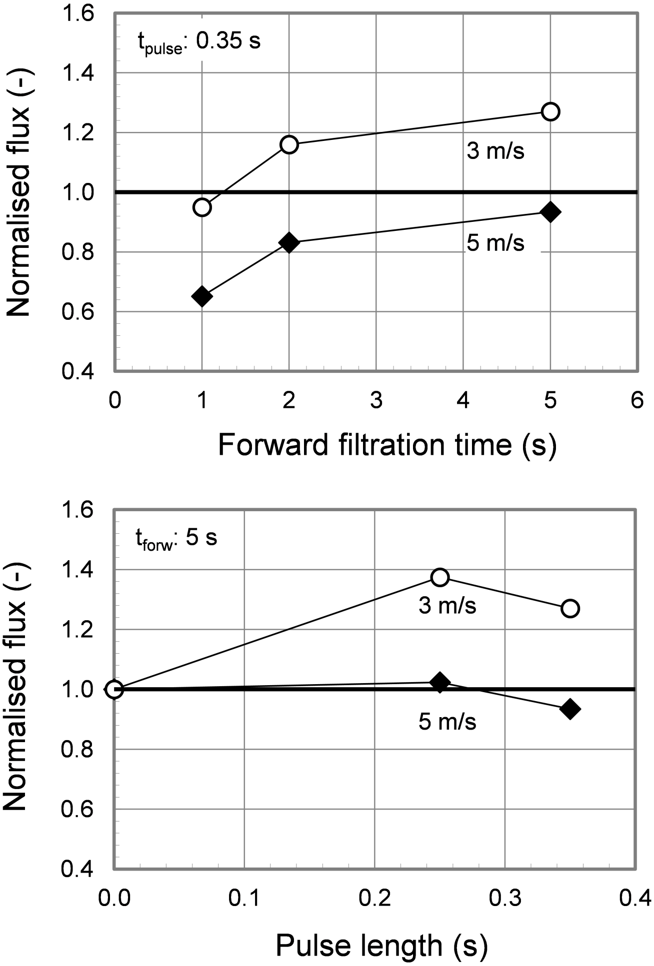

Figure 5.7: Influence of forward filtration time (t_{forw}) (above) and pulse length (t_{pulse}) (below) on normalised flux during microfiltration of TMP process water (Paper II). Normalised flux is the ratio between the fluxes observed with and without backpulsing at the same cross-flow velocity and transmembrane pressure. The temperature was 80°C.

5.2 Separation of hemicelluloses and lignin

After the removal of suspended matter and colloids, ultrafiltration can be used to concentrate the hemicelluloses and separate them from impurities such as lignin, monosaccharides and salts. Ideally, hemicelluloses should be completely retained in this stage, while the impurities pass freely through the pores of the membrane, providing the highest possible yield, concentration and purity of hemicelluloses, and thus the most valuable product. Furthermore, a high flux is desirable in order to reduce the cost of separation. The performance of four different membranes was investigated with respect to flux and retention (unpublished data), and the best membrane was used for concentration in the first ultrafiltration stage of the processes illustrated in Figure 5.1 (Papers I and III).

5.2.1 Screening of membranes

The characteristics of the membranes tested (all from Alfa Laval Nakskov A/S) for the ultrafiltration stage are given in Table 5.3. Two of these membranes (UFX5pHt, ETNA10PP) have previously been found to be suitable for the separation of hemicelluloses and lignin in microfiltered TMP process water [43, 69]. In the present work, the permeate from the microfiltration of CTMP process water was used as the feed solution. The study was carried out with flat-sheet membranes in laboratory equipment consisting of four cross-flow modules connected in parallel (the equipment is described in Paper VI). The cross-flow velocity was 0.9 m/s, and the temperature was either 60°C or 50°C, depending on the temperature tolerance of the membranes.

Table 5.3: Characteristics of the membranes used in the screening study.

Membrane	Material	Cut-off (kDa)	Max. temp. (°C)
RC70PP	Regenerated cellulose acetate	10	60
ETNA10PP	Composite fluorpolymer	10	60
UFX5pHt	Hydrophilised polysulphone	5	75
NF99HF	Polyamide on polyester	—[a]	50

[a] >98% $MgSO_4$ retention

Among the four membranes, RC70PP had highest flux in the pressure interval investigated, as can be seen in Figure 5.8. The flux was high already at a low transmembrane pressure of 4 bar, and increased only moderately above this value. Similar observations were made for the UFX5pHt membrane. Both these membranes should therefore be operated at a transmembrane pressure below 6 bar in order to reduce the risk of fouling. The flux obtained with the ETNA10PP and the NF99HF membranes was much lower at low transmembrane pressure, but increased almost linearly in the pressure interval investigated. The limiting flux had therefore not been reached, indicating that these membranes can be operated at a higher transmembrane pressure.

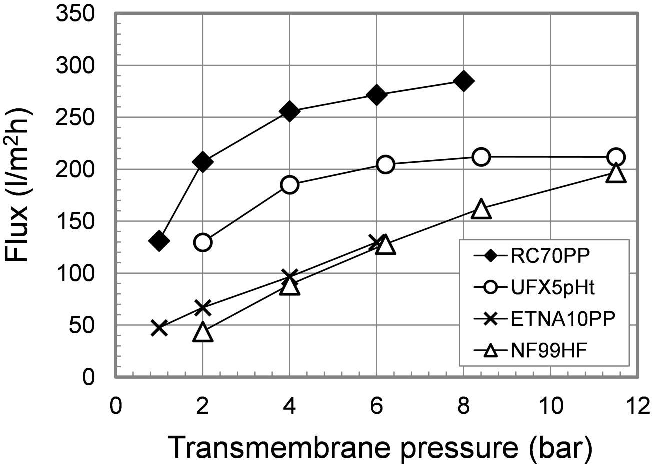

Figure 5.8: Influence of transmembrane pressure on flux for the four membranes investigated in the screening study (unpublished results). The permeate from the microfiltration of CTMP process water was used as feed solution. Retentate and permeate were recirculated to the feed tank.

Figure 5.9 shows the retention of hemicelluloses and lignin for the four membranes. The retention of both hemicellulose and lignin was very high with the NF99HF membrane, showing that the separation of these two components would not be possible with this membrane. Such separation could be achieved with the other three membranes, but only UFX5pHt had a sufficiently high hemicellulose retention. Ultrafiltration to a volume reduction of 97% with the UFX5pHt membrane would theoretically lead to the recovery of 67% of the hemicelluloses, and a concentration of 20 g/l would be achieved in the retentate. The hemicellulose yield with the ETNA10PP and RC70PP membranes would be less than 40%, and the concentration only 9.5 and 12 g/l, respectively. The UFX5pHt membrane was therefore chosen for the further investigations in which hemicelluloses were concentrated by ultrafiltration.

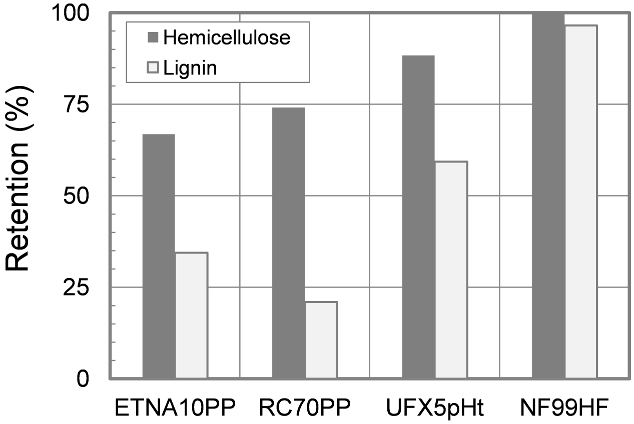

Figure 5.9: Retention of hemicelluloses and lignin at a transmembrane pressure of 6 bar with the four membranes investigated in the screening study (unpublished results).

5.2.2 Ultrafiltration performance during concentration

A spiral-wound UFX5pHt membrane element was used for the concentration of hemicelluloses by ultrafiltration, as this was assumed to be the most cost-efficient type of membrane in a large-scale process. Experiments were carried out with permeates from the microfiltration of both TMP and CTMP process water. The cross-flow rate, the transmembrane pressure and the temperature of the process streams are given in Papers I and III.

The behaviour of the flux during the concentration of hemicelluloses was similar for the two process streams, as shown in Figure 5.10 (however, note the difference in operating conditions). In both cases, a marked flux decline was observed with increasing concentration of hemicelluloses in the retentate. A high concentration of macromolecules leads to an increase in osmotic pressure, and can also result in the formation of a gel layer. Both phenomena cause a reduction in flux according to Eqs. 4.4 and 4.5. It can be seen in Figure 5.10 that, for both process streams, the flux decline was initially well described by the film model (Eq. 4.8), but a deviation from the linear relationship between flux and logarithm of the bulk concentration occurred at high concentration (above ~5 g/l). Pritchard et al. [94] observed a similar deviation during the concentration of macromolecule solutions, and showed that the deviation is the result of changes in the mass transfer coefficient when viscosity increases.

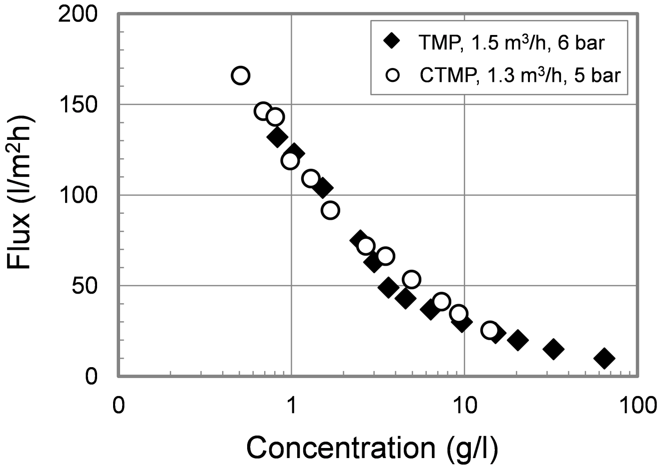

Figure 5.10: Flux during the concentration of microfiltered TMP and CTMP process water using the UFX5pHt ultrafiltration membrane (Papers I and III). The temperatures used were 80°C and 60°C for microfiltered TMP and CTMP process water, respectively.

The hemicellulose retention was high during ultrafiltration of both process streams and differed considerably from the lignin retention, as can be seen in Figure 5.11. Consequently, concentration and purification of hemicelluloses was achieved in the retentate. The UFX5pHt membrane separated hemicelluloses and lignin more efficiently in TMP process water than in CTMP process water. A possible explanation of this could be structural differences in the macromolecules in the two process streams. In the CTMP process, hemicelluloses become partly deacetylated, while lignin is sulphonated to some extent before dissolution [40, 41]. These reactions do not take place in the TMP process [39, 40]. Furthermore, hemicelluloses and lignin in CTMP process water may be interconnected to a higher degree. The existence of such lignin-carbohydrate complexes has been demonstrated previously [95, 96], and would explain the poorer separation performance during membrane filtration.

The concentration and purity of hemicelluloses in the final retentate obtained from TMP process water were 64 g/l and 59%, which are similar to the concentrations and purities in hemicellulose fractions reported by others [69, 73, 78]. In the present work, the concentration of CTMP process water was discontinued at a hemicellulose concentration of 14 g/l (purity 37%), although a higher concentration could have been achieved. This was done as a hemicellulose concentration in the range 10-20 g/l was expected to result in the most efficient enzymatic treatment using Configuration II (Petri Oinonen, private communication).

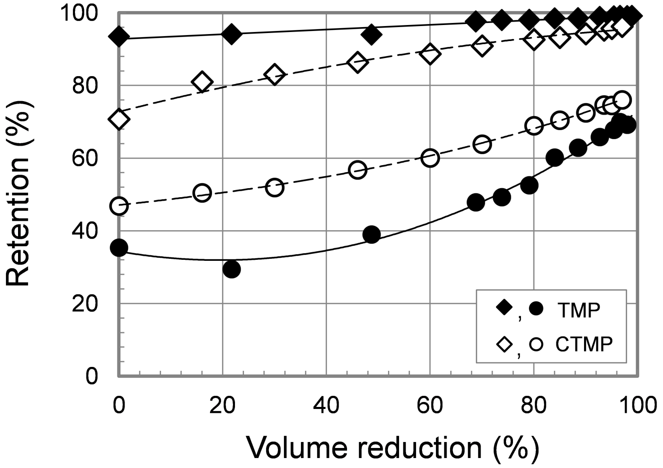

Figure 5.11: Retention of hemicelluloses (diamonds) and lignin (circles) during the concentration of microfiltered TMP and CTMP process water using the UFX5pHt ultrafiltration membrane (Papers I and III).

5.3 Cross-linking and hemicellulose fractionation

Hemicelluloses with high molecular mass will probably be needed for the manufacture of future hemicellulose-based products such as barrier films and coatings. Therefore, it may be necessary to increase the molecular mass of the hemicelluloses in pulp mill process water. The ultrafiltration retentate from CTMP process water was treated with the laccase enzyme for this purpose (Paper III). This method was developed and patented by Henriksson et al. [97], and was recently successfully applied to increase the size of various wood hemicelluloses [98]. The mechanism consists of enzyme-catalysed oxidation of the lignin end groups that are attached to hemicelluloses during the formation of radicals. The radicals subsequently couple the hemicelluloses, thereby permanently increasing their molecular mass. Figure 5.12 shows the molecular mass distribution of hemicelluloses before and after enzymatic treatment of the ultrafiltration retentate, demonstrating the desired increase in the average molecular mass of hemicelluloses.

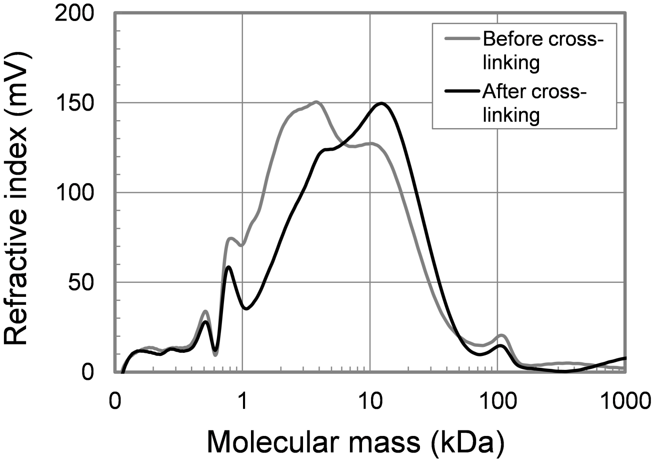

Figure 5.12: Size distribution of hemicelluloses before and after enzymatic cross-linking with laccase (Paper III). Enzymatic treatment was carried out for 3 h at a pH of 4.5 and a temperature of 40°C. Pure oxygen was continuously bubbled through the solution.

Lignin moieties are not attached to all the hemicelluloses in CTMP process water, and thus only some hemicellulose molecules are involved in cross-linking reactions. The solution obtained after enzymatic treatment is thus a mixture of cross-linked and unreacted hemicelluloses with a broad size distribution. Ultrafiltration of the solution after cross-linking was studied using a spiral-wound UFX10pHt element (cut-off 10 kDa, Alfa Laval Nakskov A/S). The aim was to remove small hemicelluloses from the mixture and to concentrate the hemicelluloses with high molecular mass in the retentate. Such fractionation allows purified hemicelluloses of particularly high molecular mass and narrow size distribution to be obtained as a product.

Most of the hemicelluloses in the solution after enzymatic treatment were recovered in the retentate, as hemicelluloses were highly retained by the membrane during fractionation (retention 90%). Thus, the concentration of hemicelluloses in the retentate increased to 53 g/l, while it was low in the permeate (about 3 g/l). As expected, the hemicelluloses in the retentate were significantly larger than those in the permeate, as can be seen in Figure 5.13. Furthermore, the hemicelluloses had a narrower size distribution than before fractionation, due to the removal of small molecules. An interesting observation was also the high viscosity of the retentate (27 mPa s at 60°C and 100 s^{-1}), which was significantly higher than the viscosity of a similar galactoglucomannan solution reported by Xu et al. [99]. The high viscosity found in the present work is probably the consequence of the altered polysaccharide structure due to cross-linking.

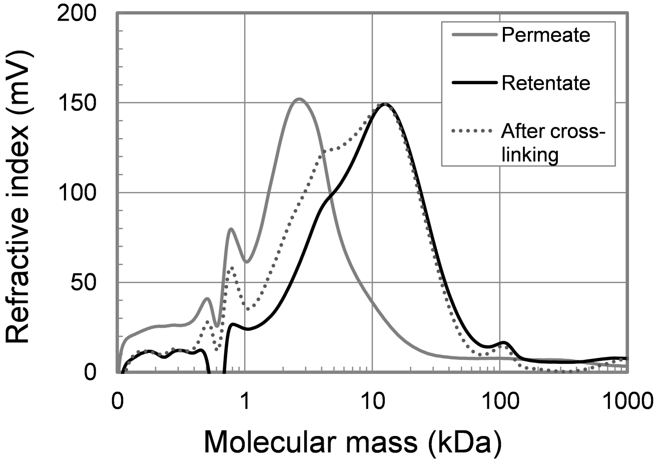

Figure 5.13: Size distribution of hemicelluloses in the high (retentate) and low (permeate) molecular mass fractions after fractionation and in the solution before fractionation (after cross-linking) (Paper III). The fractionation process was carried out by ultrafiltration using a UFX10pHt membrane.

The differences in the quality of the hemicelluloses in the two mass fractions suggest that they would be suitable for use in different applications. The retentate (high molecular mass fraction) could be suitable for high-value products such as barrier films and coatings, while the permeate (low molecular mass fraction) might be useful in applications with lower value, for example, the production of biogas or bioethanol, or as an additive during paper making in order to increase the strength of the paper. It has been shown that the molecular mass of hemicelluloses is less critical for use in the paper-making industry [92]. However, further concentration of hemicelluloses in the permeate will be required.

5.4 Pure water recovery

In the process stages common to both Configuration I & II (Figure 5.1) most organic material is removed from the pulp mill process water, leaving only small solutes (lignin, monosaccharides and salts) and especially water in the ultrafiltration permeate. Removing the residual solids, thereby producing a reusable pure water stream could also be of interest, considering that the mechanical pulping process requires as much as 10-30 m^3 of fresh water per ton of pulp produced

[100]. The recycling of purified process water to the pulp mill presupposes a high water quality, as the pulping process must not be affected detrimentally. Nanofiltration was studied as a possible technique to purify the permeate after ultrafiltration of TMP process water (Paper I). The NF99HF membrane with a magnesium sulphate retention of >98% was used for this purpose. Among the four membranes tested, this membrane has previously shown the best performance with respect to flux and retention during the purification of process water from a TMP mill [101].

About three-quarters of the initial volume of process water could be recovered as purified water by nanofiltration. However, although the initial flux was relatively high (78 l/m^2h), the average flux was only 27 l/m^2h as the flux declined rather rapidly with increasing volume reduction as a result of the increasing osmotic pressure. At a volume reduction of 76% the flux was less than 3 l/m^2h, indicating that the recovery of large amounts of purified water from the ultrafiltration permeate is not economically feasible.

The concentration of monosaccharides, lignin and ions (measured in terms of conductivity) in the ultrafiltration permeate was substantially reduced by nanofiltration, showing that the membrane retained these residual solids to a large extent. At the initial volume reduction (VR 0%), the conductivity was, for example, reduced from 2 to less than 0.2 mS/cm, and the concentration of monosaccharides and lignin was almost zero. However, the quality of the permeate decreased with increasing volume reduction. It can be seen in Figure 5.14 that conductivity and lignin concentration in the permeate increased, particularly when the volume reduction exceeded 60%. Mänttäri et al. [102] also observed an increase in ion concentration (chloride) in the permeate at higher concentration factors during the nanofiltration of water from a paper machine. They explained this observation by the Donnan exclusion mechanism, which implies that an electrical potential difference across the membrane arises as a result of the high retention of ions carrying the same charge as the membrane. This electrical potential affects the retention of charged components by the membrane. From the results of this study it can be concluded that, apart from a higher average flux, higher water quality can also be achieved by discontinuing nanofiltration at an earlier stage, i.e. at a volume reduction below 60%.

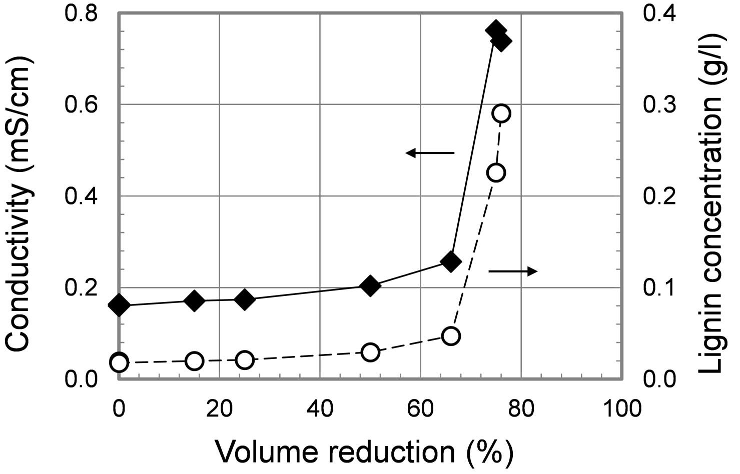

Figure 5.14: Conductivity and lignin concentration in the permeate during water purification by nanofiltration (data from Paper I). Nanofiltration was carried out with the NF99HF membrane at a temperature of 50°C, a cross-flow rate of 1.1 m^3/h and a transmembrane pressure of 20 bar.

Nanofiltration of pulp and paper effluents has also been studied by other researchers with the intention of water conservation and reuse. The performance of various membranes has, for example, been investigated with wastewater resulting from paper production [102–105] and water discharged from external activated sludge processes [106]. A large-scale nanofiltration plant for the purification of paper machine water has been installed at the M-Real Kirkniemi paper mill in Finland [106].

Chapter 6

Separation of components in alkaline extract

A separation process was developed to recover hemicelluloses and chemicals from an alkaline extract from wheat bran. The process is schematically illustrated in Figure 6.1. After extraction of the target molecules with NaOH, hemicelluloses were separated from the extraction chemical and co-extracted organic substances by ultrafiltration. A concentrated and purified hemicellulose fraction was obtained in the retentate, while the extraction chemical remained in the permeate together with a small amount of organic substances. These impurities were removed by nanofiltration, resulting in a purified NaOH solution that could be recycled and reused for extraction. An alternative to this process is to add a pre-filtration stage prior to ultrafiltration, as shown in Figure 6.1. The intention of pre-filtration is to remove substances that hinder ultrafiltration, thereby improving ultrafiltration performance. The major product of this process is the ultrafiltration retentate containing the hemicelluloses. These molecules were further processed by our project partner in order to manufacture biodegradable barrier films for food packaging.

The ultrafiltration and nanofiltration stages of the process were investigated in detail in this work. The aim was to optimise the entire separation process by studying, for example, the influence of the operating conditions and the use of pre-filtration on ultrafiltration performance. Various membranes were tested in the nanofiltration stage, and the cost of recovering the extraction chemical was estimated. This chapter deals with the results obtained in these investigations. The findings presented and discussed here are taken mainly from Papers IV, V and VI.

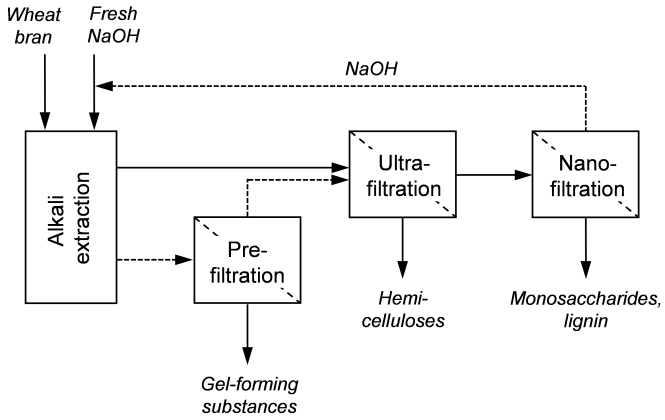

Figure 6.1: Schematic illustration of the separation process used to recover hemicelluloses and chemicals from an alkaline extract from wheat bran. NaOH was used for the extraction of hemicelluloses in the alkali extraction stage.

6.1 Separation of hemicelluloses and the extraction chemical

In order to solubilise hemicelluloses in wheat bran at high yield during alkali extraction, a large amount of the extraction chemical is required. The concentration of NaOH in the alkaline extract is therefore substantial (about 40 g/l), constituting almost 80% of the total solids. Hemicelluloses are present at a concentration of about 7.9 g/l, being only the second most prevalent substance. Before being used in high-value applications, the hemicelluloses must be separated from the extraction chemical and purified. For this purpose, a tubular ceramic ultrafiltration membrane with a cut-off of 10 kDa (Atech Innovations GmbH) was used (Papers IV and V).

A major challenge during the separation of hemicelluloses and the extraction chemical is the high viscosity of the alkaline extract, which is about 14 times the viscosity of water. Generally, when treating high-viscosity solutions with membrane filtration the flux is low [94, 107, 108], and the pressure drop along the membrane module is high. A larger membrane area is thus required for filtration, the separation performance can be reduced, and more energy is required for circulation [109]. For these reasons, the best performance during the ultrafiltration of the alkaline extract will presumably be achieved by operating under conditions at which the viscosity of the solution is as low as possible. Such a reduction in viscosity can be achieved either by optimising the viscosity-influencing operating conditions, or by removing substances responsible for the high viscosity prior to ultrafiltration. Both these strategies were evaluated and their influence on ultrafiltration performance was studied.

6.1.1 Influence of operating conditions

Investigation of the physical properties of the alkaline extract revealed that the viscosity was markedly influenced by the temperature and the shear stress (Paper IV). Increasing the temperature, for example, from 50 to 80°C decreased the viscosity to less than half. Furthermore, the solution was found to exhibit shear-thinning rheological behaviour, which means that the viscosity decreases with increasing shear stress. Therefore, temperature and cross-flow velocity will be important parameters during ultrafiltration. The influence of both parameters was studied at constant transmembrane pressure with the 10 kDa ceramic membrane (Paper IV). Both the retentate and permeate stream were recirculated in order to maintain constant concentration in the feed tank.

The ultrafiltration flux is shown as a function of the cross-flow velocity at two different temperatures in Figure 6.2. As expected, a considerably higher flux was achieved at the higher temperature. Moreover, the flux was found to increase almost linearly with increasing cross-flow velocity. The flux-enhancing effect of

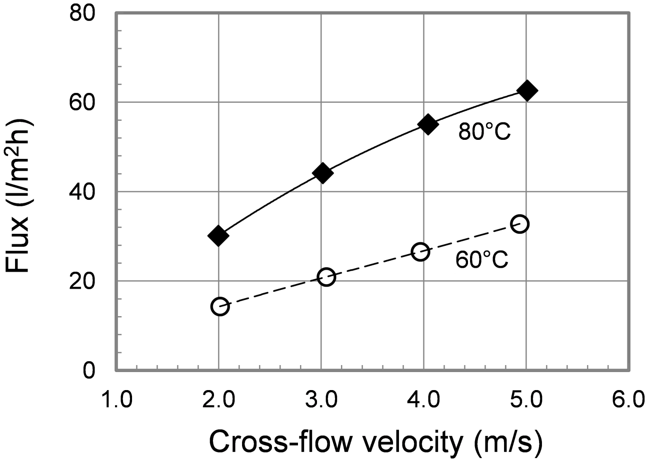

Figure 6.2: Influence of cross-flow velocity on flux during ultrafiltration of an alkaline extract from wheat bran at two temperatures (Paper IV). A tubular ceramic membrane with a cut-off of 10 kDa was used for filtration, and the transmembrane pressure was maintained at 1.5 bar.

high temperature can be attributed to the decrease in viscosity. High cross-flow velocity is presumably beneficial due to the sheer-thinning rheological behaviour and the fact that deposited substances can be more efficiently removed from the membrane surface. The highest temperature investigated was 80°C, although the results indicate that a higher flux might be achieved by increasing the temperature further. However, too high a temperature could lead to degradation of the hemicelluloses [26], which would reduce their suitability as a feedstock for high-value products.

A higher flux can often be achieved by increasing the transmembrane pressure during ultrafiltration since this increases the force driving filtration. The influence of transmembrane pressure on ultrafiltration performance was therefore studied at constant temperature using three different cross-flow velocities (Paper V). The flux during ultrafiltration of the alkaline extract was affected by the transmembrane pressure, but no significant improvement in flux was seen upon increasing the pressure. As can be seen in Figure 6.3, even at the highest cross-flow velocity of 5 m/s, the flux levelled off at a low transmembrane pressure (about 0.8 bar), after which it became increasingly independent of pressure. This levelling-off of the flux indicates that some substances in the alkaline extract formed a gel layer on the membrane surface. As the formation of such a layer could not be avoided even at the highest shear, it appears that it is impossible to

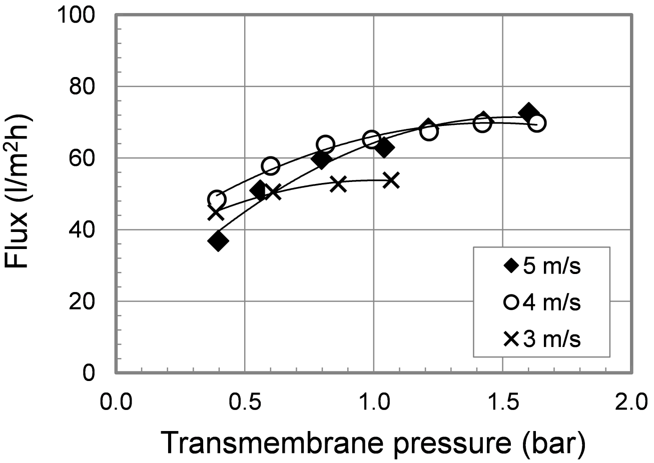

Figure 6.3: Influence of transmembrane pressure on flux during ultrafiltration of an alkaline extract from wheat bran at a temperature of 80°C (Paper V), using a tubular ceramic membrane with a cut-off of 10 kDa.

achieve a flux above 75 l/m^2h in the ultrafiltration stage by simply optimising the operating conditions. The flux during ultrafiltration of similar hemicellulose-containing extracts has been studied by others using various kinds of membranes and modules [17, 19, 76, 107], and low flux seems to be a common problem with this kind of process stream.

The retention of the membrane was not affected by varying the temperature, cross-flow velocity or transmembrane pressure during ultrafiltration. The retention of hemicelluloses was high (about 96%) and the retention of NaOH less than 10%. Thus, from a separation point of view, ultrafiltration of the alkaline extract was most satisfactory.

6.1.2 Influence of pre-filtration

The addition of a pre-filtration stage to the process was investigated with the aim of improving the subsequent ultrafiltration performance. Appropriate pretreatment can improve flux during membrane filtration, as shown by others [72, 110, 111]. Furthermore, pretreatment may be advantageous as it might also increase the purity of the hemicellulose fraction after ultrafiltration, and thereby its suitability for the manufacture of barrier films. Apart from hemicelluloses and the extraction chemical, the alkaline extract also contains acid-insoluble substances. In the initial experiments it was found that about 90% of these compounds was retained by the ultrafiltration membrane (Paper V). As a consequence of this high retention, a considerable proportion of these acid-insoluble substances will end up in the ultrafiltration retentate together with the hemicelluloses. Contamination of the product could possibly be prevented by the removal of such compounds using pre-filtration. Two different methods, microfiltration and dead-end filtration in a filter press with kieselguhr as filter aid, were used in this work. The pore size of the microfiltration membrane was 0.2 μm, and a 10 μm filter cloth was used in the filter press. The influence on ultrafiltration performance was studied after pre-filtration using the microfiltration permeate and the dead-end filtration filtrate as feed in the ultrafiltration stage of the process.

Both pre-filtration methods increased the ultrafiltration flux substantially, as can be seen in Figure 6.4. The highest flux achieved when treating the solution obtained from the extraction process, was only about 75 l/m^2h, while the flux obtained at the same operating conditions after dead-end filtration and microfiltration was 225 and 440 l/m^2h, respectively. The limiting flux during ultrafiltration of the two filtrates was not reached in the pressure interval investigated, indicating that substances that formed a deposition layer were removed to a large extent by both pre-filtration methods. The removal of these gel-forming substances, in combination with the markedly lower viscosity of the solutions after pre-filtration (Paper V), is probably the reason for the positive effect on ultrafiltration flux.

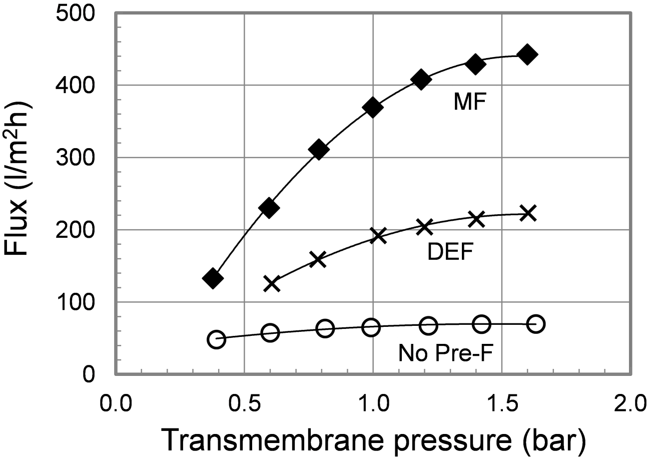

Figure 6.4: Flux in the ultrafiltration stage of the process after either microfiltration (MF), dead-end filtration (DEF) or no pre-filtration (No Pre-F) of the alkaline extract from wheat bran (data from Paper V). A tubular ceramic membrane with a cut-off of 10 kDa was used for ultrafiltration. The temperature was 80°C and the cross-flow velocity 4 m/s.

Although microfiltration led to the greatest improvement in the flux, this method is not suitable for pre-filtration, if carried out in the same way as in this work. It was found that the hemicellulose concentration after microfiltration was only 4% of the initial concentration in the extract. The 0.2 μm membrane thus retained most of the hemicelluloses, leading to a substantial product loss. One way of making microfiltration more suitable could be to use a membrane with a larger pore size. However, the fact that hemicellulose molecules are much smaller than the 0.2 μm pores suggests that macromolecules were retained by the gel layer. Therefore, decreasing the membrane resistance by increasing the pore size may not lead to the desired decrease in retention. The observation that membrane pore size is not always a key factor in improving retention efficiency has also been made by Liu et al. [112].

The loss in hemicelluloses using dead-end filtration was negligible, and more than half of the undesired acid-insoluble substances could be removed. Thus, dead-end filtration has the potential to increase the cost-efficiency of hemicellulose recovery from the alkaline extract. However, it should be noted that a large amount of kieselguhr was needed as a filter aid in order to achieve acceptable capacity and filtrate purity. The concentration of filter aid (2 wt%) was more than 10 times the concentration typically used in industry, for example, for the clarification of beer [113]. This large amount of kieselguhr leads to an increase in process cost and a high burden on the environment. Therefore, there is clearly a need to optimise the pre-filtration stage.

The impact of dead-end filtration on the quality of oxygen barrier films produced from isolated hemicelluloses was further investigated by our project partner (unpublished results). Barrier films for food packaging with a thickness of 50 μm were prepared from hemicelluloses isolated by ultrafiltration and from hemicelluloses isolated by a combination of dead-end filtration and ultrafiltration. The strength of both kinds of free-standing films was evaluated by measuring the tensile strain at break. The capability of the films to retain oxygen gas when used to coat a polyethylene terephthalate support was also measured. It was found that films produced from hemicelluloses isolated by dead-end filtration had a tensile strain at break more than twice as high (28.2% versus 12.6%), but the same low oxygen transmission rate ($\sim$5 cm^3 m^{-2} d^{-1} measured at 50% relative humidity) as those manufactured from hemicelluloses isolated by ultrafiltration alone. Thus, it appears that as well as improving membrane performance, dead-end filtration also increases the quality of the final product. The tensile strain at break and oxygen transmission rates of the films prepared in this work were comparable to those prepared by others [6–8].

6.1.3 Ultrafiltration performance during concentration

The performance of ultrafiltration during the concentration of hemicelluloses in the alkaline extract was investigated (Paper V). The major objective of this study was to determine the maximal achievable hemicellulose concentration in the retentate. Furthermore, it was of interest to analyse the influence of concentration on the flux. The alkaline extract was pre-filtered in the filter press prior to ultrafiltration.

The flux is shown as a function of hemicellulose concentration in the retentate in Figure 6.5. As expected, the flux declined with increasing concentration, and it was found that this behaviour was well described by the film model (Eq. 4.8). The maximal hemicellulose concentration achievable in the retentate can thus be determined to be about 40-50 g/l, which was reported to be the gelation concentration of arabinoxylan [107]. The final retentate still contained more NaOH than hemicelluloses, which suggests that purification of the hemicelluloses after concentration will be necessary. This could be achieved by diafiltration

[68], precipitation with organic solvents [74] or chromatographic methods [80, 88].

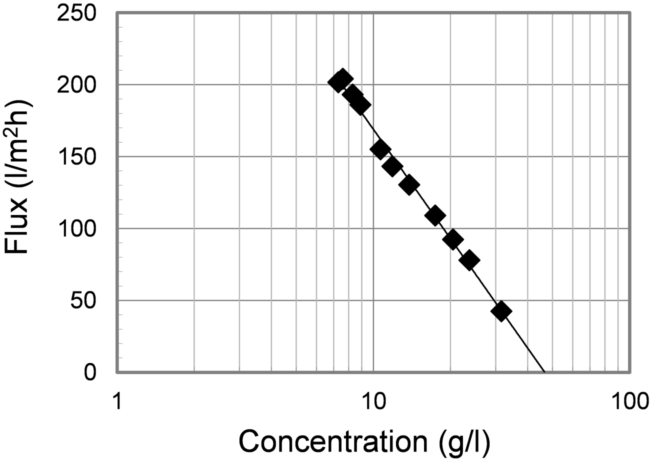

Figure 6.5: Flux during the concentration of hemicelluloses in alkaline extract after dead-end filtration. A tubular ceramic membrane with a cut-off of 10 kDa was used for ultrafiltration (data from Paper V). The temperature was 80°C, the cross-flow velocity 5 m/s and the transmembrane pressure 1.2 bar.

6.2 Separation of the extraction chemical and residual solids

Most of the organic substances were removed from the alkaline extract in the prefiltration and ultrafiltration stages. As a consequence, almost 95% of the solids in the ultrafiltration permeate consisted of NaOH, and only 5% represented organic substances such as lignin and monosaccharides. Removing this minor amount of organic material could allow reuse of the process stream for hemicellulose extraction, leading to savings in the cost of the extraction chemical. Nanofiltration has been used for the recovery of caustic solutions, for example, from process liquors from viscose fibre production [114], from cleaning solutions in the dairy industry [115, 116], and from wastewater in polyester or chitin processing [117, 118]. Nanofiltration was also studied in the present work (Paper VI). First, a suitable membrane for NaOH recovery was identified in a screening study. Then, the best membranes were further investigated in a concentration study, and the cost-efficiency of NaOH recovery by nanofiltration was evaluated.

6.2.1 Screening of nanofiltration membranes

During nanofiltration of the ultrafiltration permeate, organic substances must be retained by the membrane to high degree in order to prevent the accumulation of organic material when recycling the alkaline solution. In contrast, a low retention of NaOH is desirable, since the higher the concentration in the permeate, the less the amount of fresh extraction chemical required in order to regain the initial strength of the extraction solution. The performance of seven membranes, differing in cut-off and material, was investigated. The main characteristics of these membranes are given in Paper VI.

The separation performance and the flux differed considerably between the membranes included in the study. It can be seen in Figure 6.6 that only the membranes manufactured by Koch Systems Inc. (MPF-34, MPF-36) and Microdyn Nadir GmbH (NP030, NP010) showed sufficiently high retention of lignin and sugars to be suitable for this application. The highest removal of organic substances was achieved with the MPF-34 membrane, with which the retention of both lignin and sugars was above 99.5%. This membrane is thus most suitable if there is a high demand on the purity of the NaOH solution during reuse. However, the MPF-34 membrane also retained NaOH to a high degree, leading to a reduction in the amount of extraction chemical that can be recovered in the permeate. Furthermore, it had the disadvantage of a relatively low flux.

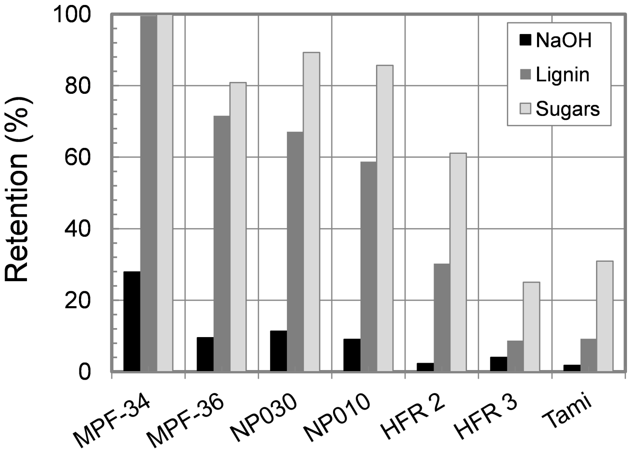

Figure 6.6: Separation performance of various nanofiltration membranes for the recovery of NaOH from the permeate after ultrafiltration (Paper VI). The permeate and the retentate stream were recirculated to the feed tank.

The flux during nanofiltration of the alkaline solution was considerably higher than expected for some membranes, based on previously published data for this kind of application. Fluxes in the range of 7-50 l/m^2h have been measured by other researchers during the recovery of NaOH from alkaline solutions by nanofiltration [114–118]. In the present work, a flux of this magnitude ($\sim$25 l/m^2h) was only observed for the MPF-34 membrane. In the case of the NP030 membrane the flux was $\sim$190 l/m^2h, and with the NP010 and MPF-36 membranes a flux of almost 500 l/m^2h was achieved under the most suitable operating conditions (Paper VI). These exceptionally high fluxes are probably the result of the efficient removal of organic substances in the previous stages of the process. Van der Bruggen et al. [111] showed that large organic compounds could have a considerable negative impact on flux during nanofiltration.

Due to their high flux and good separation performance, the MPF-36 and the NP010 membranes were further investigated. The aim of these experiments was to study the performance of nanofiltration during concentration of the alkaline solution, and to obtain data for the cost estimates.

6.2.2 Nanofiltration performance during concentration

A similar high average flux (about 200 l/m^2h) was observed during concentration of the alkaline solution to a volume reduction of 75% with the NP010 and MPF-36 membranes (Paper VI). The initial flux was higher with NP010, while the flux was found to decline less with increasing volume reduction with MPF-36. The less pronounced flux decline with MPF-36 indicates that this membrane is less susceptible to fouling and would thus presumably require less frequent cleaning when used in a large-scale process. However, the NP010 membrane has the advantage of having a higher temperature tolerance. As high temperature was found to be an advantage in the ultrafiltration stage of the process, using a membrane resistant to high temperature during nanofiltration would obviate the need for cooling prior to nanofiltration.

The alkaline solution could be purified to about the same extent with both membranes without any significant loss in the extraction chemical, as can be seen in Figure 6.7. The retention of NaOH was below 20% (averaged value) in both cases, resulting in a recovery of almost 70% in the nanofiltration permeate. The recovery of NaOH could be increased even further by allowing nanofiltration to proceed to a higher volume reduction. However, as lignin and sugars are not completely retained by these membranes, the amount of impurities in the nanofiltration permeate would also increase with increasing volume reduction. The concentration of NaOH in the permeate accumulated after nanofiltration was found to be about 35.7 g/l for the MPF-36 membrane and 37.7 g/l for the NP010 membrane. Considering that the concentration of NaOH in the alkaline solution used for hemicellulose extraction is roughly 40 g/l, the need for fresh NaOH to restore the solution prior to reuse would be small, and thus the potential saving in the cost of the extraction chemical considerable.

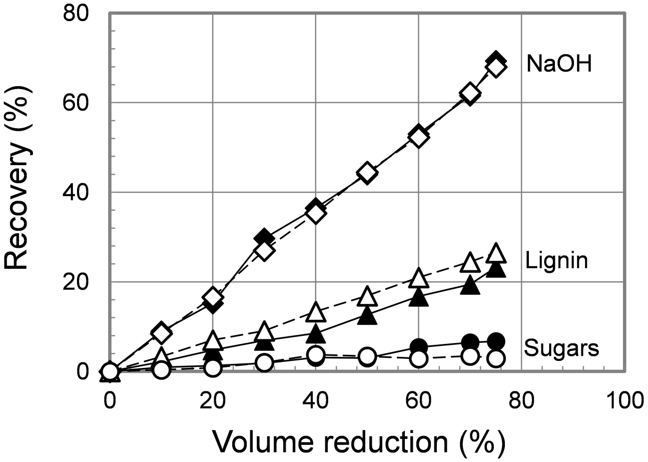

Figure 6.7: Recovery of NaOH, lignin and sugars in the nanofiltration permeate during concentration using the MPF-36 membrane (filled symbols) and the NP010 membrane (open symbols). The cross-flow velocity was 0.9 m/s, the transmembrane pressure 15 bar, and the temperature 70°C (MPF-36) or 80°C (NP010). (Data from Paper VI).

6.2.3 Cost of recovering the extraction chemical

Recovering NaOH from the ultrafiltration permeate for reuse reduces the cost of the chemical needed for the extraction of hemicelluloses from wheat bran, but increases the investment and operating costs for membrane filtration since an additional nanofiltration stage is required for the purification of the permeate. Calculations were therefore performed to determine whether the cost savings resulting from additional nanofiltration could compensate for the additional expense. The cost estimates were based on empirical data from a concentration study carried out with the NP010 membrane, as well as cost data obtained from membrane manufacturers. Further details of the assumptions made in the cost estimates can be found in Paper VI.

The estimates indicated that the application of the nanofiltration stage in the process illustrated in Figure 6.1 is cost-efficient, provided that the entire nanofiltration permeate can be reused for extraction. The investment cost for a nanofiltration plant capable of recovering about 0.3 tons of NaOH per hour was estimated to be 123 k€ . The membrane area required in this plant is about 57 m^2 and the operating costs only 5.6 € per ton dry NaOH dissolved in the nanofiltration permeate. As the price of NaOH purchased in large quantities is 350 € per ton, the investment cost of such a membrane plant would be paid back after less than 1150 hours of operation.

It should be pointed out that the cost estimates presented in Paper VI are based on flux data obtained with flat-sheet membranes, while the nanofiltration plant was designed for spiral-wound elements by reason of their lower cost. It is not certain that the same flux would be achieved with spiral elements as with flat-sheet membranes, as fluid dynamics can vary considerably in different modules. Ribera et al. [119] compared nanofiltration using the same membrane in flat-sheet and spiral-wound configurations and obtained very similar results. However, Räsänen et al. [120] found that the flux during nanofiltration with flat-sheet membranes was about twice as high as that with a spiral-wound element, and assumed that this was because the entire membrane area was not used effectively in the spiral element. Thus, although the nanofiltration plant considered in the present work was provided with a safety margin of 25 m^2 (45% of the required membrane area), a larger plant may be needed in a commercial process, resulting in a higher investment cost and a longer payback time. Therefore, the conclusion that can be drawn from the cost estimates is that the use of nanofiltration has a high cost-reducing potential, but additional experiments are needed for final dimensioning and reliable cost estimates for a large-scale plant.

Chapter 7

Conclusions and future work

Many industrial processes using biomass as raw material result in process streams in which components such as hemicelluloses, lignin and extractives are dissolved or dispersed. These biopolymers have a high potential for use as a resource for new bio-based products. The work described in this thesis was concerned with the separation of these biomass components from each other, thereby producing concentrated, purified fractions suitable for new products. Separation processes were developed for two process streams originating from thermomechanical and chemithermomechanical pulping of wood, as well as for an alkaline solution derived from an industrial process in which hemicelluloses are extracted from wheat bran. The influence of various process parameters and process configurations on separation performance was studied in order to make separation as energy- and cost-efficient as possible.

7.1 Conclusions

Microfiltration was found to be an efficient method for separating undissolved substances from dissolved macromolecules in both types of pulp mill process water. Using this technique, it was possible to remove suspended solids and colloidal wood extractives almost completely. A high flux and low fouling tendency were achieved with a membrane with a pore size of 0.2 μm. However, the retention of dissolved hemicelluloses was relatively high, reducing the amount of hemicelluloses that could be recovered from TMP and CTMP process water. Although hemicellulose retention was reduced by increasing the membrane pore size, 0.4 and 0.8 μm membranes are not suitable for this application due to their high susceptibility to pore blockage.

It was shown that the operating conditions had a marked influence on flux during microfiltration, but did not affect retention. A higher flux was achieved by increasing the cross-flow velocity from 3 to 5 m/s and by increasing the transmembrane pressure in the range 0.3 to ~1.0 bar. A volume reduction of at least 98% could be achieved at high average flux (260-300 l/m^2h) with both types of process water, as shown in the concentration studies. Allowing microfiltration to proceed to high volume reduction is important, as it allows an acceptably high yield of hemicelluloses to be achieved, despite elevated retention by the membrane. In the experimental studies, almost 80% of the hemicelluloses could be recovered in the microfiltration permeate.

During the microfiltration of TMP process water backpulsing was found to increase the flux by 40% at the lower cross-flow velocity of 3 m/s, provided that appropriate backpulsing parameters were used. This indicates that microfiltration could be operated at a lower cross-flow velocity with backpulsing, without the undesirable decline in flux. Such a reduction in cross-flow velocity is attractive as it decreases the energy required by the recirculation pumps, and could therefore increase the cost-efficiency of microfiltration. However, the technique was not efficient in reducing the high retention of hemicelluloses.

The separation of dissolved hemicelluloses and lignin molecules in the microfiltration permeate by ultrafiltration was studied. Of four different polymeric membranes, the UFX5pHt membrane (cut-off 5 kDa) showed the best separation performance and exhibited a high flux and a relatively low fouling tendency. It was shown that hemicelluloses in TMP process water could be concentrated to above 60 g/l and that the purity could be increased to about 60%, due to the efficient removal of lignin molecules with the ultrafiltration permeate. Using enzymatic treatment after hemicellulose concentration, it was possible to cross-link hemicelluloses in CTMP process water, thereby increasing their molecular mass. It was found that hemicelluloses with high molecular mass could be partially separated from those with low molecular mass using an additional ultrafiltration stage after cross-linking. Enzymatic treatment followed by hemicellulose fractionation is particularly attractive if large molecules with a narrow size distribution are needed for the manufacture of new bio-based products.

Results from the studies carried out on the alkaline extract from wheat bran showed that hemicelluloses could be efficiently separated from the main impurity, NaOH, by ultrafiltration using a 10 kDa ceramic membrane. However, the high viscosity of the solution and the presence of gel-forming substances resulted in an unacceptably low flux. The flux could be increased by increasing the temperature and cross-flow velocity, but increasing the transmembrane pressure above 0.8 bar had only a slight flux-enhancing effect. Furthermore, the results indicated that a flux above 75 l/m^2h could not be achieved by simply optimising the operating conditions during ultrafiltration. Studies of pre-filtration methods showed that the viscosity could be substantially reduced and gel-forming substances partly removed prior to ultrafiltration. As a result of this, the ultrafiltration flux increased to 225 and 440 l/m^2h after pre-filtration by dead-end filtration and microfiltration, respectively. However, although microfiltration resulted in the most pronounced improvement in flux, only dead-end filtration allowed high hemicellulose recovery in the separation process.

Purification of the ultrafiltration permeate by nanofiltration was studied with the aim of producing a purified NaOH solution that could be reused for hemicellulose extraction. It was shown that an extremely high flux (almost 500 l/m^2h) could be combined with very low NaOH retention (3-15%) and good removal of organic impurities (retention of lignin and sugars of 52-89%) when using the polymeric membranes NP010 (cut-off $\sim$1.2 kDa) and MPF-36 (cut-off 1 kDa) for nanofiltration. Use of the MPF-34 membrane (cut-off 0.2 kDa) resulted in a purer NaOH solution, which could be a requirement for reuse, however, less NaOH could be recovered due to the higher retention, and the flux was more than a factor 10 lower than that obtained with the NP010 and MPF-36 membranes. Preliminary cost estimates based on experimental data obtained with the NP010 membrane indicated that the investment cost of a nanofiltration plant would be paid back after only 1150 hours of operation.

7.2 Future work

This work dealt primarily with the development of separation processes for various biomass-containing process streams. However, very little work has been performed on investigating the most suitable application for the concentrated and purified fractions obtained in these separation processes. More extensive studies of the properties of the high-value products that could be manufactured from these fractions should be carried out in the future.

During the microfiltration of pulp mill process water a high flux was achieved, but the retention of hemicelluloses was also high although the molecules are smaller than the pores of the membrane. In this work it was hypothesised that agglomeration and adsorption were the main causes of the elevated retention, but no proof was presented. Further investigations into the cause of increased retention and ways of preventing it would be beneficial, as this would allow higher hemicellulose yields to be achieved in the separation process.

Backpulsing was found to have the potential for energy savings during the microfiltration of pulp mill process water, as it would allow operation at lower cross-flow velocities. However, more detailed investigations are needed to determine the optimal backpulsing parameters, and studies of the technique at low cross-flow velocity in a concentration study with TMP and CTMP process water remain to be done. Results from such investigations would be interesting as they would allow a reliable determination of the energy-saving potential of backpulsing.

Recovering biomass components such as hemicelluloses and lignin from pulp mill process water alters the composition of these streams. In a pulp mill the process water is partly recirculated for washing purposes before it leaves the mill as waste water. Changing the composition of the recirculation water could affect the pulping process and the pulp quality. Future studies must address this issue before separation processes developed for pulp mill process water can be implemented on a large scale.

In the process developed for treating alkaline extract from wheat bran, the use of dead-end filtration was found to enhance the performance of subsequent ultrafiltration. However, as dead-end filtration was not optimised, the capacity was rather low and the amount of kieselguhr needed was high. More detailed investigations are needed, including studies on the influence of using various kieselguhr qualities, filter cloth structures and operating conditions, to optimise the performance of dead-end filtration. High centrifugal forces could possibly also be effective in removing gel-forming substances, thereby improving the ultrafiltration flux without the need of a filter aid. The use of centrifugation as a possible form of pretreatment prior to ultrafiltration was not considered in the present work, but should be investigated in the future.

When using the NP010 and MPF-36 membranes, a purified solution of the extraction chemical was produced after ultrafiltration of the alkaline extract from wheat bran. This solution was intended to be reused for hemicellulose extraction, thereby reducing the amount of NaOH required in the entire process. In the future, it should be investigated whether the nanofiltration permeate is of sufficient purity for reuse, and how recirculation would affect the overall process. Furthermore, nanofiltration studies should be carried out using spiral-wound elements in order to confirm the cost estimates presented in this work.

The experimental studies presented in this thesis were carried out on large laboratory scale. Working on this scale provides valuable information on suitable membranes and operating conditions, as well as appropriate process configurations. However, pilot-scale experiments will be required to verify the results and refine the process design. Such investigations are also needed to study the long-term performance of the membrane filtration stages and to determine the cost of the process more precisely. Furthermore, pilot experiments should be used to investigate how the separation processes developed in this work could be integrated into existing processes at industrial sites.

References

[1] International panel on climate change (IPCC), "IPCC fourth assessment report (AR4) - climate change 2007: Synthesis report," 2007.

[2] D. Fengel and G. Wegener, *Wood - chemistry, ultrastructure, reactions*. Walter de Gruyter GmbH & Co. KG, 1989.

[3] B. Hahn-Hägerdal, M. Galbe, M. F. Gorwa-Grauslund, G. Lidén, and G. Zacchi, "Bio-ethanol - the fuel of tomorrow from the residues of today," *TRENDS in Biotechnology*, vol. 24, no. 12, pp. 549–556, 2006.

[4] A. J. Ragauskas, M. Nagy, D. H. Kim, C. A. Eckert, J. P. Hallett, and C. L. Liotta, "From wood to fuels - integrating biofuels and pulp production," *Industrial Biotechnology*, vol. 2, no. 1, pp. 55–65, 2006.

[5] M. Henriksson, L. A. Berglund, P. Isaksson, T. Lindström, and T. Nishino, "Cellulose nanopaper structures of high toughness," *Biomacromolecules*, vol. 9, no. 6, pp. 1579–1585, 2008.

[6] M. Gröndahl, L. Eriksson, and P. Gatenholm, "Material properties of plasticized hardwood xylans for potential application as oxygen barrier films," *Biomacromolecules*, vol. 5, no. 4, pp. 1528–1535, 2004.

[7] N. M. L. Hansen and D. Plackett, "Sustainable films and coatings from hemicelluloses: A review," *Biomacromolecules*, vol. 9, no. 6, pp. 1493–1505, 2008.

[8] J. Hartman, A.-C. Albertsson, M. Söderqvist-Lindblad, and J. Sjöberg, "Oxygen barrier materials from renewable sources: Material properties of softwood hemicellulose-based films," *Applied Polymer Science*, vol. 100, no. 4, pp. 2985–2991, 2006.

[9] I. Gabrielii and P. Gatenholm, "Preparation and properties of hydrogels based on hemicellulose," *Applied Polymer Science*, vol. 69, no. 8, pp. 1661–1667, 1998.

[10] I. Gabrielii, P. Gatenholm, W. G. Glasser, R. K. Jain, and L. Kenne, "Separation, characterization and hydrogel-formation of hemicellulose from aspen wood," *Carbohydrate Polymers*, vol. 43, no. 4, pp. 367–374, 2000.

[11] T. Hannuksela, B. Holmbom, G. Mortha, and D. Lachenal, "Effect of sorbed galactoglucomannans and galactomannans on pulp and paper handsheet properties, especially strength properties," *Nordic Pulp and Paper Journal*, vol. 19, no. 2, pp. 237–244, 2004.

[12] S. Willför, K. Sundberg, M. Tenkanen, and B. Holmbom, “Spruce-derived mannans - a potential raw material for hydrocolloids and novel advanced natural materials,” *Carbohydrate Polymers*, vol. 72, no. 2, pp. 197–210, 2008.

[13] W. F. Broekaert, C. M. Courtin, K. Verbeke, T. van de Wiele, W. Verstraete, and J. A. Delcour, “Prebiotic and other health-related effects of cereal-derived arabinoxylans, arabinoxylan-oligosaccharides, and xylooligosaccharides,” *Critical Reviews in Food Science and Nutrition*, vol. 51, no. 2, pp. 178–194, 2011.

[14] M. Kleinert and T. Barth, “Towards a lignocellulosic biorefinery: direct one-step conversion of lignin to hydrogen-enriched biofuel,” *Energy and Fuels*, vol. 22, no. 2, pp. 1371–1379, 2008.

[15] J. F. Kadla, S. Kubo, R. A. Venditti, R. D. Gilbert, A. L. Compere, and W. Griffith, “Lignin-based carbon fibers for composite fiber applications,” *Carbon*, vol. 40, no. 15, pp. 2913–2920, 2002.

[16] F. Bertaud and B. Holmbom, “Chemical composition of earlywood and latewood in Norway spruce heartwood, sapwood and transition zone wood,” *Wood Science and Technology*, vol. 38, no. 4, pp. 245–256, 2004.

[17] R. Zeitoun, P. Y. Pontalier, P. Marechal, and L. Rigal, “Twin-screw extrusion for hemicellulose recovery: Influence on extract purity and purification performance,” *Bioresource Technology*, vol. 101, no. 23, pp. 9348–9354, 2010.

[18] J. Söderström, L. Pilcher, M. Galbe, and G. Zacchi, “Two-step steam pretreatment of softwood by diluted H_2SO_4 impregnation for ethanol production,” *Biomass and Bioenergy*, vol. 24, no. 6, pp. 475–486, 2003.

[19] L. Jacquemin, R. Zeitoun, C. Sablayrolles, P. Y. Pontalier, and L. Rigal, “Evaluation of the technical and environmental performances of extraction and purification processes of arabinoxylans from wheat straw and bran,” *Process Biochemistry*, vol. 47, no. 3, pp. 373–380, 2012.

[20] M. Bataillon, P. Mathaly, A.-P. Nunes-Cardinali, and F. Duchiron, “Extraction and purification of arabinoxylan from destarched wheat bran in a pilot scale,” *Industrial Crops and Products*, vol. 8, no. 1, pp. 37–43, 1998.

[21] R. M. Brown, “Cellulose structure and biosynthesis: What is in store for the 21st century,” *Journal of Polymer Science*, vol. 42, no. 3, pp. 487–495, 2004.

[22] E. Sjöström, *Wood chemistry - Fundamentals and applications (Second Edition)*. Academic press Limited, 1993.

[23] H. V. Scheller and P. Ulvskov, *Annual review of plant biology - Hemicelluloses*. Annual Reviews, 2010.

[24] S. Willför, A. Sundberg, J. Hemming, and B. Holmbom, “Polysaccharides in some industrially important softwood species,” *Wood Science and Technology*, vol. 39, no. 4, pp. 245–257, 2005.

[25] S. Willför, A. Sundberg, A. Pranovich, and B. Holmbom, “Polysaccharides in some industrially important hardwood species,” *Wood Science and Technology*, vol. 39, no. 8, pp. 601–617, 2005.

[26] A. Ebringerová and T. Heinze, “Xylan and xylan derivatives - biopolymers with valuable properties, 1,” *Macromolecular Rapid Communications*, vol. 9, no. 6, pp. 1493–1505, 2008.

[27] J. Lundqvist, A. Teleman, L. Junel, G. Zacchi, O. Dahlman, F. Tjerneld, and H. Stålbrand, “Isolation and characterization of galactoglucomannan from spruce (Picea abies),” *Carbohydrate Polymers*, vol. 48, no. 1, pp. 29–39, 2002.

[28] S. Willför, R. Sjöholm, C. Laine, M. Roslund, J. Hemming, and B. Holmbom, “Characterisation of water-soluble galactoglucomannans from Norway spruce wood and thermomechanical pulp,” *Carbohydrate Polymers*, vol. 52, no. 2, pp. 175–187, 2003.

[29] M. S. Izydorczyk and C. G. Biliaderis, “Cereal arabinoxylans: advances in structure and physicochemical properties,” *Carbohydrate Polymers*, vol. 28, no. 1, pp. 33–48, 1995.

[30] M. Ek, G. Gellerstedt, and G. Henriksson, *Pulp and Paper Chemistry and Technology*, ch. 6, vol. 1. Walter de Gruyter GmbH & Co. KG, 2009.

[31] J. J. Meister, “Modification of lignin,” *Journal of Macromolecular Science*, vol. 42, no. 2, pp. 235–289, 2002.

[32] R. Alén, V.-P. Moilanen, and E. Sjöström, “Potential recovery of hydroxy acids from kraft pulping liquors,” *Tappi Journal*, vol. 69, no. 2, pp. 76–78, 1986.

[33] H. Niemi, J. Lahti, H. Hatakka, S. Kärki, S. Rovio, M. Kallioinen, M. Mänttäri, and M. Louhi-Kultanen, “Fractionation of organic and inorganic compounds from black liquor by combining membrane separation and crystallization,” *Chemical Engineering Technology*, vol. 34, no. 4, pp. 593–598, 2011.

[34] S. Hellstén, J. Lahti, J. Heinonen, M. Kallioinen, M. Mänttäri, and T. Sainio, “Purification process for recovering hydroxy acids from soda black liquor,” *Chemical Engineering Research and Design (http://dx.doi.org/10.1016/j.cherd.2013.06.001)*, 2013.

[35] A. Marcus, “LignoBoost: A greener future,” *Paper360°*, pp. 30–32, May 2008.

[36] Metso Corporation, “Press release: Metso-supplied world’s first commercial LignoBoost plant successfully starts up at Domtar in the USA.” Available at `http://www.metso.com`, 2013 [accessed 03.06.13].

[37] M. Ek, G. Gellerstedt, and G. Henriksson, *Pulp and Paper Chemistry and Technology*, ch. 4, vol. 2. Walter de Gruyter GmbH & Co. KG, 2009.

[38] H. Sixta, *Handbook of pulp - Volume 2*. Wiley-VCH Verlag GmbH & Co. KGaA, 2006.

[39] J. Thornton, R. Ekman, B. Holmbom, and F. Örså, "Polysaccharides dissolved from Norway spruce in thermomechanical pulping and peroxide bleaching," *Wood Chemistry and Technology*, vol. 14, no. 2, pp. 159–175, 1994.

[40] J. Konn, A. Pranovich, and B. Holmbom, "Dissolution of fibre material in alkaline pre-treatment and refining of spruce CTMP," *Holzforschung*, vol. 60, no. 12, pp. 32–39, 2006.

[41] J. Konn, B. Holmbom, and O. Nickull, "Chemical reactions in chemithermomechanical pulping: Material balances of wood components in a CTMP process," *Pulp and Paper Science*, vol. 28, no. 1, pp. 395–399, 2003.

[42] A. V. Pranovich, K. E. Sundberg, and B. R. Holmbom, "Chemical changes in thermomechanical pulp at alkaline conditions," *Wood Chemistry and Technology*, vol. 23, no. 1, pp. 89–112, 2003.

[43] T. Persson and A.-S. Jönsson, "Isolation of hemicelluloses by ultrafiltration of thermomechanical pulp mill process water - influence of operating conditions," *Chemical Engineering Research & Design*, vol. 88, no. 12A, pp. 1548–1554, 2010.

[44] A. V. Pranovich and M. Reunanen, "Dissolved lignin and other aromatic substances in thermomechanical pulp waters," *Wood Chemistry and Technology*, vol. 25, no. 3, pp. 109–132, 2005.

[45] M. E. F. Bergmans, G. Beldman, H. Gruppen, and A. G. J. Voragen, "Optimisation of the selective extraction of (glucurono)arabinoxylans from wheat bran: Use of barium and calcium hydroxide solution at elevated temperatures," *Cereal Science*, vol. 23, no. 3, pp. 235–245, 1996.

[46] J. M. Fang, R. C. Sun, D. Salisbury, P. Fowler, and J. Tomkinson, "Comparative study of hemicelluloses from wheat straw by alkali and hydrogen peroxide extractions," *Polymer Degradation and Stability*, vol. 66, no. 3, pp. 423–432, 1999.

[47] M. E. F. Schooneveld-Bergmans, A. M. C. P. Hopman, G. Beldman, and A. G. J. Voragen, "Extraction and partial characterization of feruloylated glucuronoarabinoxylans from wheat bran," *Carbohydrate Polymers*, vol. 35, no. 1-2, pp. 39–47, 1997.

[48] W. G. Glasser, W. E. Kaar, R. K. Jain, and J. E. Sealey, "Isolation options for non-cellulosic heterosaccharides (HetPS)," *Cellulose*, vol. 7, no. 3, pp. 299–317, 2000.

[49] A. Höije, M. Gröndahl, K. Tømmeraas, and P. Gatenholm, “Isolation and characterization of physicochemical and material properties of arabinoxylans from barley husks,” *Carbohydrate Polymers*, vol. 61, no. 3, pp. 266–275, 2005.

[50] A. A. Roos, T. Persson, H. Krawczyk, G. Zacchi, and H. Stålbrand, “Extraction of water-soluble hemicelluloses from barley husks,” *Bioresearch Technology*, vol. 100, no. 2, pp. 763–769, 2009.

[51] R. C. Sun, J. Tomkinson, P. L. Ma, and S. F. Liang, “Comparative study of hemicelluloses from rice straw by alkali and hydrogen peroxide treatments,” *Carbohydrate Polymers*, vol. 42, no. 2, pp. 111–122, 2000.

[52] R. C. Sun, J. M. Fang, and J. Tomkinson, “Characterization and esterification of hemicelluloses from rye straw,” *Agricultural and Food Chemistry*, vol. 48, no. 4, pp. 1247–1252, 2000.

[53] T. Song, A. Pranovich, I. Sumerskiy, and B. Holmbom, “Extraction of galactoglucomannan from spruce wood with pressurised hot water,” *Holzforschung*, vol. 62, no. 6, pp. 659–666, 2008.

[54] T. Persson, J. L. Ren, E. Joelsson, and A.-S. Jönsson, “Fractionation of wheat and barley straw to access high-molecular-mass hemicelluloses prior to ethanol production,” *Bioresource Technology*, vol. 100, no. 17, pp. 3906–3913, 2009.

[55] F. Peng, P. Peng, F. Xu, and R.-C. Sun, “Fractional purification and bioconversion of hemicelluloses,” *Biotechnology Advances*, vol. 30, no. 4, pp. 879–903, 2012.

[56] T. Hannuksela and B. Holmbom, “Stabilization of wood-resin emulsions by dissolved galactoglucomannans and galactomannans,” *Journal of Pulp and Paper Science*, vol. 30, no. 6, pp. 159–164, 2004.

[57] M. Cheryan, *Ultrafiltration and microfiltration handbook*. Technomic Publishing Co., Inc., 1998.

[58] M. Y. Jaffrin, “Dynamic shear-enhanced membrane filtration: A review of rotating disks, rotating membranes and vibrating systems,” *Journal of Membrane Science*, vol. 324, no. 1-2, pp. 7–25, 2008.

[59] A. Guerra, G. Jonsson, A. Rasmussen, E. Waagner-Nielsen, and D. Edelsten, “Low cross-flow velocity microfiltration of skim milk for removal of bacterial spores,” *International Dairy Journal*, vol. 7, no. 12, pp. 849–861, 1997.

[60] Q. Gan, J. A. Howell, R. W. Field, R. England, M. R. Bird, C. L. O’Shaughnessy, and M. T. MeKechinie, “Beer clarification by microfiltration - product quality control and fractionation of particles and macromolecules,” *Journal of Membrane Science*, vol. 194, no. 2, pp. 185–196, 2001.

[61] J. Cakl, I. Bauer, P. Doleček, and P. Mikulášek, "Effects of backflushing conditions on permeate flux in membrane crossflow microfiltration of oil emulsion," *Desalination*, vol. 127, no. 2, pp. 189–198, 2000.

[62] R. Sondhi and R. Bhave, "Role of backpulsing in fouling minimization in crossflow filtration with ceramic membranes," *Journal of Membrane Science*, vol. 186, no. 1, pp. 41–52, 2001.

[63] J. A. Levesley and M. Hoare, "The effect of high frequency backflushing on the microfiltration of yeast homogenate suspensions for the recovery of soluble proteins," *Journal of Membrane Science*, vol. 158, no. 1-2, pp. 29–39, 1999.

[64] C. S. Parnham and R. H. Davis, "Protein recovery from bacterial cell debris using crossflow microfiltration with backpulsing," *Journal of Membrane Science*, vol. 118, no. 2, pp. 259–268, 1996.

[65] A.-S. Jönsson, A.-K. Nordin, and O. Wallberg, "Concentration and purification of lignin in hardwood kraft pulping liquor by ultrafiltration and nanofiltration," *Chemical Engineering Research and Design*, vol. 86, no. 11A, pp. 1271–1280, 2008.

[66] A. Toledano, L. Serrano, A. Garcia, I. Mondragon, and J. Labidi, "Comparative study of lignin fractionation by ultrafiltration and selective precipitation," *Chemical Engineering Journal*, vol. 157, no. 1, pp. 93–99, 2010.

[67] O. Wallberg, *Extraction of lignin from kraft cooking liquor by ultrafiltration*. PhD thesis, Department of Chemical Engineering, Lund University, Sweden, 2005.

[68] A. Andersson, T. Persson, G. Zacchi, H. Stålbrand, and A.-S. Jönsson, "Comparison of diafiltration and size-exclusion chromatography to recover hemicelluloses from process water from thermomechanical pulping of spruce," *Applied Biochemistry and Biotechnology*, vol. 137, pp. 971–983, 2007.

[69] T. Persson, A.-K. Nordin, G. Zacchi, and A.-S. Jönsson, "Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce," *Applied Biochemistry and Biotechnology*, vol. 137, pp. 741–752, 2007.

[70] S. Willför, P. Rehn, A. Sundberg, K. Sundberg, and B. Holmbom, "Recovery of water-soluble acetylgalactoglucomannans from mechanical pulp of spruce," *Tappi Journal*, vol. 2, no. 11, pp. 27–32, 2003.

[71] M. J. González-Munõz, S. Rivas, V. Santos, and J. C. Parajó, "Fractionation of extracted hemicellulosic saccharides from Pinus pinaster wood by multistep membrane processing," *Journal of Membrane Science*, vol. 428, pp. 281–289, 2013.

[72] E. Koivula, M. Kallioinen, S. Preis, L. Testova, H. Sixta, and M. Mänttäri, “Evaluation of various pretreatment methods to manage fouling in ultrafiltration of wood hydrolysates,” *Separation and Purification Technology*, vol. 83, pp. 50–56, 2011.

[73] M. Al Manasrah, M. Kallioinen, H. Ilvesniemi, and M. Mänttäri, “Recovery of galactoglucomannan from wood hydrolysate using regenerated cellulose ultrafiltration membranes,” *Bioresource Technology*, vol. 114, pp. 375–381, 2012.

[74] T. Song, A. Pranovich, and B. Holmbom, “Separation of polymeric galactoglucomannans from hot-water extract of spruce wood,” *Bioresource Technology*, vol. 130, pp. 198–203, 2013.

[75] H. Krawczyk, T. Persson, and A.-S. Jönsson, “Isolation of hemicelluloses from barley husks,” *Food and Bioproducts Processing*, vol. 86, no. C1, pp. 31–36, 2008.

[76] R. Vegas, A. Moure, H. Domínguez, J. C. Parajó, J. R. Alvarez, and S. Luque, “Evaluation of ultra- and nanofiltration for refining soluble products from rice husk xylan,” *Bioresource Technology*, vol. 99, no. 13, pp. 5341–5351, 2008.

[77] A. Sundberg, S. Willför, P. Rehn, and B. Holmbom, “Can water-soluble O-acetyl-galactoglucomannans be isolated in large-scale from TMP?,” in *Proceedings 12th International Symposium on Wood and Pulping Chemistry (Vol. 2)*, University of Wisconsin-Madison, 2003.

[78] T. Persson and A.-S. Jönsson, “Fouling of ultrafiltration membranes during isolation of hemicelluloses in the forestry industry,” *Scholarly Research Exchange*, vol. 2009, no. ID 624012, pp. 1–7, 2009.

[79] J. Hollmann and M. G. Lindhauer, “Pilot-scale isolation of glucuronoarabinoxylans from wheat bran,” *Carbohydrate Polymers*, vol. 59, no. 2, pp. 225–230, 2005.

[80] R. Vegas, S. Luque, J. R. Alvarez, J. L. Alonso, H. Domínguez, and J. C. Parajó, “Membrane-assisted processing of xylooligosaccharide-containing liquors,” *Agricultural and Food Chemistry*, vol. 54, no. 15, pp. 5430–5436, 2006.

[81] I. Egüés, C. Sanchez, I. Mondragon, and J. Labidi, “Separation and purification of hemicellulose by ultrafiltration,” *Industrial & Engineering Chemical Research*, vol. 51, no. 1, pp. 523–530, 2012.

[82] L. Puro, M. Kallioinen, M. Mänttäri, G. Natarajan, D. C. Cameron, and M. Nyström, “Performance of RC and PES ultrafiltration membranes in filtration of pulp mill process waters,” *Desalination*, vol. 264, no. 3, pp. 249–255, 2010.

[83] L. Puro, M. Kallioinen, M. Mänttäri, and M. Nyström, “Evaluation of behavior and fouling potential of wood extractives in ultrafiltration of pulp

and paper mill process water," *Journal of Membrane Science*, vol. 368, no. 1-2, pp. 150–158, 2011.

[84] A. Hasan, R. Yasarla, B. V. Ramarao, and T. E. Amidon, "Separation of lignocellulosic hydrolyzate components using ceramic microfilters," *Wood Chemistry and Technology*, vol. 31, no. 4, pp. 357–383, 2011.

[85] H. Wallmo, H. Theliander, A.-S. Jönsson, and O. Wallberg, "The influence of hemicelluloses during the precipitation of lignin in kraft black liquor," *Nordic Pulp and Paper Research Journal*, vol. 24, no. 2, pp. 165–171, 2009.

[86] Y. He, D. M. Bagely, K. T. Leung, S. N. Liss, and B.-Q. Liao, "Recent advances in membrane technologies for biorefining and bioenergy production," *Biotechnology Advances*, vol. 30, no. 4, pp. 817–858, 2012.

[87] W. L. McCabe, J. C. Smith, and P. Harriott, *Unit operations of chemical engineering*. McGraw-Hill Book Co., 2001.

[88] N. Westerberg, H. Sunner, M. Helander, G. Henriksson, M. Lawoko, and A. Rasmuson, "Separation of galactoglucomannans, lignin, and lignin-carbohydrate complexes from hot-water-extracted Norway spruce by cross-flow filtration and adsorption chromatography," *Bioresources*, vol. 7, no. 4, pp. 4501–4516, 2012.

[89] K. Swennen, C. M. Courtin, B. van der Bruggen, C. Vandecasteele, and J. A. Delcour, "Ultrafiltration and ethanol precipitation for isolation of arabinoxylooligosaccharides with different structures," *Carbohydrate Polymers*, vol. 62, no. 3, pp. 283–292, 2005.

[90] G. Liu, Y. Liu, J. Ni, H. Shi, and Y. Qian, "Treatability of kraft spent liquor by microfiltration and ultrafiltration," *Desalination*, vol. 160, no. 2, pp. 131–141, 2004.

[91] J. D. Blake and G. N. Richards, "Evidence for molecular aggregation in hemicelluloses," *Carbohydrate Research*, vol. 18, no. 1, pp. 11–21, 1971.

[92] T. Hannuksela, M. Tenkanen, and B. Holmbom, "Sorption of dissolved galactoglucomannans and galactomannans to bleached kraft pulp," *Cellulose*, vol. 9, no. 3-4, pp. 251–261, 2002.

[93] I. A. Johnsen, P. Stenius, T. Tammelin, M. Österberg, L.-S. Johansson, and J. Laine, "The influence of dissolved substances on resin adsorption to TMP fine material," *Nordic Pulp and Paper Research*, vol. 21, no. 5, pp. 629–637, 2006.

[94] M. Pritchard, J. A. Howell, and R. W. Field, "The ultrafiltration of viscous fluids," *Journal of Membrane Science*, vol. 102, pp. 223–235, 1995.

[95] M. Lawoko, G. Henriksson, and G. Gellerstedt, "Characterization of lignin-carbohydrate complexes from spruce sulfite pulp," *Holzforschung*, vol. 60, no. 2, pp. 162–165, 2006.

[96] M. Lawoko, G. Henriksson, and G. Gellerstedt, “Characterization of lignin-carbohydrate complexes (LCCs) of spruce wood (Picea abies L.) isolated with two methods,” *Holzforschung*, vol. 60, no. 2, pp. 156–161, 2006.

[97] G. Henriksson, D. Areskogh, and P. Oinonen, “A method to increase the molecular weight of wood mannans and xylans comprising aromatic moieties,” *PCT/WO2012071004*, vol. Patent, 2012.

[98] P. Oinonen, D. Areskogh, and G. Henriksson, “Enzyme catalyzed cross-linking of spruce galactoglucomannan improves its applicability in barrier films,” *Carbohydrate Polymers*, vol. 95, no. 2, pp. 690–696, 2013.

[99] C. Xu, S. Willför, P. Holmlund, and B. Holmbom, “Rheological properties of water-soluble spruce O-acetyl galactoglucomannans,” *Carbohydrate Polymers*, vol. 75, no. 3, pp. 498–504, 2009.

[100] D. Pokhrel and T. Viraraghavan, “Treatment of pulp and paper mill wastewater - a review,” *Science of the Total Environment*, vol. 333, no. 1-3, pp. 37–58, 2004.

[101] T. Persson and A.-S. Jönsson, “Purification of process water in a thermomechanical pulp mill by nanofiltration.” *Report LUTKDH/(TKKA-7001)/1-7/(2009)*, Department of Chemical Engineering, Lund University, Sweden, 2009.

[102] M. Mänttäri, J. Nuortila-Jokinen, and M. Nyström, “Evaluation of nanofiltration membranes for filtration of paper mill total effluent,” *Filtration & Separation*, vol. 34, no. 3, pp. 275–280, 1997.

[103] M. Mänttäri, J. Nuortila-Jokinen, and M. Nyström, “Influence of filtration conditions on the performance of NF membranes in the filtration of paper mill total effluent,” *Journal of Membrane Science*, vol. 137, no. 1-2, pp. 187–199, 1997.

[104] J. Nuortila-Jokinen and M. Nyström, “Comparison of membrane separation processes in the internal purification of paper mill water,” *Journal of Membrane Science*, vol. 119, no. 1, pp. 99–115, 1996.

[105] M. Pizzichini, C. Russo, and C. D. Meo, “Purification of pulp and paper wastewater with membrane technology for water reuse in a closed loop,” *Desalination*, vol. 178, no. 1-3, pp. 351–359, 2005.

[106] M. Mänttäri, K. Viitikko, and M. Nyström, “Nanofiltration of biologically treated effluents from the pulp and paper industry,” *Journal of Membrane Science*, vol. 272, no. 1-2, pp. 152–160, 2006.

[107] J. Jorda, P. Marechal, L. Rigal, and P.-Y. Pontalier, “Biopolymer purification by ultrafiltration,” *Desalination*, vol. 148, no. 1-3, pp. 187–191, 2002.

[108] W. Shu-Sen, “Effect of solution viscosity on ultrafiltration flux,” *Journal of Membrane Science*, vol. 39, no. 2, pp. 187–194, 1988.

[109] H. Krawczyk and A.-S. Jönsson, "The influence of feed flow channel diameter on frictional pressure drop, membrane performance and process cost in full-scale tubular ceramic membranes," *Chemical Engineering Research and Design (http://dx.doi.org/10.1016/j.cherd.2013.06.019)*, 2013.

[110] H. E. Cutler, S. M. Husson, and S. R. Wickramasinghe, "Prefiltration to suppress protein fouling of microfiltration membranes," *Separation and Purification Technology*, vol. 89, pp. 329–336, 2012.

[111] B. van der Bruggen, D. Segers, C. Vandecasteele, L. Braeken, A. Volodin, and C. V. Haesendonck, "How a microfiltration pretreatment affects the performance in nanofiltration," *Separation Science and Technology*, vol. 39, no. 7, pp. 1443–1459, 2005.

[112] G. Liu, Y. Liu, H. Shi, and Y. Qian, "Application of inorganic membranes in the alkali recovery process," *Desalination*, vol. 169, no. 2, pp. 193–205, 2004.

[113] N. A. Schmid, *Verbesserung der filtrationstechnischen Eigenschaften von Filterhilfsmitteln durch ein thermisches Verfahren*. PhD thesis, Lehrstuhl für Energie- und Umwelttechnik der Lebensmittelindustrie, Technische Universität München, Germany, 2002.

[114] R. Schlesinger, G. Götzinger, H. Sixta, A. Friedl, and M. Harasek, "Evaluation of alkali resistant nanofiltration membranes for the separation of hemicellulose from concentrated alkaline process liquors," *Desalination*, vol. 192, no. 1-3, pp. 303–314, 2006.

[115] S. Novalic, A. Dabrowski, and K. D. Kulbe, "Nanofiltration of caustic and acidic cleaning solutions with high COD, Part 1. recycling of sodium hydroxide," *Journal of Food Engineering*, vol. 38, no. 2, pp. 125–132, 1998.

[116] E. Räsänen, M. Nyström, J. Sahlstein, and O. Tossavainen, "Purification and regeneration of diluted caustic and acidic washing solutions by membrane filtration," *Desalination*, vol. 149, no. 1-3, pp. 185–190, 2002.

[117] E. K. Choe, E. J. Son, B. S. Lee, S. H. Jeong, H. C. Shin, and J. S. Choi, "NF process for the recovery of caustic soda and concentration of disodium terephthalate from alkaline wastewater from polyester fabrics," *Desalination*, vol. 186, no. 1-3, pp. 29–37, 2005.

[118] L. Zhao and W. Xia, "Stainless steel membrane UF coupled with NF process for the recovery of sodium hydroxide from alkaline wastewater in chitin processing," *Desalination*, vol. 249, no. 2, pp. 774–780, 2009.

[119] G. Ribera, L. Llenas, X. Martínez, M. Rovira, and J. de Pablo, "Comparison of nanofiltration membranes' performance in flat sheet and spiral wound configurations: a scale-up study," *Desalination and Water Treatment*, vol. 51, no. 1-3, pp. 458–468, 2013.

[120] E. Räsänen, M. Nyström, J. Sahlstein, and O. Tossavainen, "Comparison of commercial membranes in nanofiltration of sweet whey," *Lait*, vol. 82, no. 3, pp. 343–356, 2002.

Paper I

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Fractionation of process water in thermomechanical pulp mills

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ABSTRACT

In this work process water from a thermomechanical pulp mill was divided into five fractions by filtration and membrane filtration. Suspended matter was mainly isolated in the retentate from the drum filter, extractives in the microfiltration retentate, hemicelluloses in the ultrafiltration retentate and lignin in the nanofiltration retentate. The final water fraction was of fresh water quality. For each tonne of pulp produced, about 10 kg of suspended matter, more than 0.3 kg of extractives, 11 kg of hemicelluloses and 8 kg of aromatic compounds (lignin) could be recovered from the drum filtration retentate, the microfiltration retentate, the ultrafiltration retentate and the nanofiltration retentate, respectively. About 40% of the treated process water could be recovered as fresh water.

1. Introduction

Galactoglucomannans (GGM), which are the main hemicelluloses in softwood, could be used in a wide variety of applications (Willför et al., 2008). Examples of products that could be derived from GGM are food packaging film (Hartman et al., 2006a,b; Hansen and Plackett, 2008), hydrogels (Söderqvist Lindblad et al., 2001, 2005) and emulsion stabilizers for beverages (Mikkonen et al., 2009). It has also been proposed that GGM could be used to decrease the deposition tendency of pitch in paper pulp and increase paper strength (Willför et al., 2003a).

Several research groups have studied the recovery of GGM from Norway spruce (*Picea abies*) using different methods. Lundqvist et al. (2003) and Palm and Zacchi (2003, 2004) used heat-fractionation and steam treatment of wood chips, while Willför et al. (2003a,b) extracted GGM from native wood and thermomechanical pulp. Recently, GGM have been recovered from process streams from thermomechanical pulp (TMP) mills (Persson et al., 2007; Willför et al., 2008; Xu et al., 2009; Persson, 2009).

The yield during thermomechanical pulping is about 97.5% of the wood material (Sundholm, 1999), which means that 2.5% of the material is dissolved in the process water. GGM, which represent 15–20% of the wood in softwood, constitute the main material dissolved in water. In total about 10% of the GGM are dissolved (Thornton et al., 1994), corresponding 1–2% of the wood material. The high solubility of GGM is due to their high degree of acetylation in combination with their relatively low-molar-mass (Hartman et al., 2006a).

A schematic flow sheet illustrating a process for the recovery of non-fibrous wood material components released from thermomechanical pulps has been presented by Willför et al. (2003a). A patent for the process was filed in 2001 (Eckerman et al., 2002). In the patented process, the isolation of different substances is performed in a number of sequential stages: (1) fibres and larger particles are removed by pressing or filtration, (2) non-soluble colloidal wood resins are isolated by extraction, filtration, centrifugation or flotation, (3) aromatic compounds are removed by absorbents, aromatic exchange resin or chromatography and, finally, salts are removed by dialysis or reverse osmosis leaving a purified fraction of polysaccharides.

The process used in this work, which is based on our previous studies (Persson et al., 2007, 2009; Persson, 2009), consists of four stages. In this process, the separation of substances in TMP process water is achieved by filtration and membrane filtration only. Drum filtration (DF) is used in the first stage to remove particles and fines. Extractives and remaining suspended solids in the filtrate are removed in the second stage by microfiltration (MF). Hemicelluloses are concentrated by ultrafiltration (UF) in the third stage, and, finally, the UF permeate, containing sugar, lignin and salt, is purified by nanofiltration (NF). The aim of this work was to study the fractionation and performance of each of the four stages.

Ultrafiltration is the key technology when isolating GGM from process water in TMP mills. The performance of the UF membrane is thus of the utmost importance. Choosing a membrane is a delicate balance between capacity (flux), yield (retention) of GGM, purity of the product (retention of GGM and lignin) and fouling

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(cleaning frequency). Membranes with cut-offs of 1 kDa (Hartman et al., 2006b; Persson, 2009), 5 kDa (Persson, 2009), 10 kDa (Persson et al., 2007; Persson, 2009) and 20 kDa (Willför et al., 2003a) have been used in previous investigations. It was shown that membranes with cut-offs of 5 and 10 kDa can be operated at rather high fluxes, whereas the flux of a membrane with a cut-off of 1 kDa was significantly lower (Persson, 2009). The membrane with a cut-off of 5 kDa exhibited a higher fouling susceptibility, but higher temperature stability and retention of GGM than the 10 kDa membranes. This membrane was therefore used in this investigation.

In an industrial application, the entire process would, of course, be run continuously. In the current study, every stage had to be run separately due to the finite volume of process water. However, after the completion of one stage, the liquid was immediately treated in the next stage. Industrial conditions were thus as closely resembled as possible.

2. Methods

2.1. Process water

Process water from a Swedish TMP mill producing pulp from spruce wood was used to evaluate the fractionation process. About 920 l of process water was collected from the disc filters after the refiners and immediately transported to Lund University. Refining is performed in this mill at a pressure of about 4 bar and a temperature of 140 °C. The temperature of the process water at the time of collection was 80 °C and 50 °C at the time of delivery. The pH of the process water was 4.3. The water contained about 1.2 g/l hemicelluloses, of which GGM was the main constituent. The average molar mass has been determined in a previous study to be about 10 kDa (Persson, 2009).

2.2. Experimental procedure

The process water was divided into five fractions by filtration and membrane filtration, as shown in Fig. 1. The membrane filtration (MF, UF and NF) experiments were performed in a similar way. The MF and UF systems were first operated in semi-batch mode, i.e. the feed tank (200 l) was continuously topped up with feed solution as permeate was withdrawn. When the last of the feed solution had been added to the feed tank, the system was operated batch-wise. The NF system was operated in batch mode from the beginning.

Before membrane filtration, the systems were allowed to stabilize for 1 h at the chosen operating conditions. The flux of the MF, UF and NF membranes was then stable when concentration began. During stabilization, both the retentate and the permeate were recirculated to the feed tank. During the actual filtration run, the retentate was recycled to the feed tank and the permeate was withdrawn continuously.

Pressure was measured at the inlet and outlet of the feed channel. In the microfiltration equipment, the pressure was also measured on the permeate side. In the ultrafiltration and nanofiltration equipments, atmospheric pressure was assumed on the permeate side. The transmembrane pressure is the average pressure between the inlet and outlet pressure minus the pressure on the permeate side. During microfiltration, the transmembrane pressure was regulated by two valves, one on the retentate line and one on the permeate line. The temperature was measured with a Pt100 thermocouple element and controlled with a PID regulator. The permeate flow was measured gravimetrically with a balance. Pressure, temperature and permeate flow rate were recorded by a PC equipped with LabView 6.0 software (National Instruments Co., TX, USA). Samples were taken from the feed tank and the permeate line at different volume reduction (VR) intervals. VR is defined as the ratio between the volume of permeate withdrawn and the feed volume.

The membranes were cleaned with an alkaline cleaning agent, 0.5 wt.% Ultrasil 10 (Henkel Chemicals Ltd., Germany), for one hour at 50 °C. The system was thoroughly rinsed with deionized water after cleaning.

2.3. Drum filtration

The process water was treated in a drum filter (model HDF802-1F) from HydroTech AB, Sweden, to remove particles and fines. The pore size of the microscreen was 10 μm and the filtration area was 0.9 m^2. During rotation of the drum, the nozzles spray filtrate onto the microscreen to remove the retained solid material. The filtration rig was operated at the highest possible capacity (meaning that the drum is constantly in rotation). Filtrate was continuously withdrawn while the retained solid material was recirculated to the feed tank. Filtration was performed at 50 °C (the temperature of the process water at the time of delivery).

2.4. Microfiltration

The filtrate from drum filtration was further treated by microfiltration to remove the remaining solids and extractives. A ceramic membrane with a pore size of 0.2 μm (Atech Innovations GmbH, Germany) was used. The membrane used in the investigation is 1 m long and has seven flow channels in parallel, each with an inner diameter of 6 mm (a 7/6 element). The total membrane area is 0.13 m^2. The largest module using 7/6 elements contains 114 elements (all in parallel) giving a total membrane area of 15 m^2. In this study, a single-element module (M1) was used. Filtration was performed at 80 °C. The cross-flow velocity was 4 m/s, giving

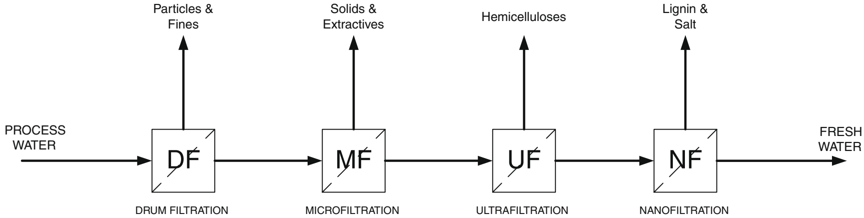

Fig. 1. A schematic illustration of the overall process.

a pressure drop over the element of 0.73 bar. The average transmembrane pressure was 0.7 bar.

2.5. Ultrafiltration

The permeate from the microfiltration stage was ultrafiltered to concentrate and purify the hemicelluloses. A 2517 UFX5 spiral-wound membrane element (Alfa Laval Corp., Sweden) with a 48 mil (1.2 mm) spacer was used. The membrane is made of hydrophilized polyethersulphone and the nominal molar mass cut-off is 5 kDa. The outer diameter of the membrane element is 2.5″ (0.06 m) and the length 17″ (0.43 m). The membrane area is 0.7 m^2.

Filtration was performed at 80 °C. The transmembrane pressure was 6 bar and the cross-flow was 1.5 m^3/h. The cross-flow did not need to be reduced during concentration as the maximum pressure drop recommended by the manufacturer (0.6 bar) was not exceeded. The pressure drop was 0.3 bar at the beginning and 0.6 bar at the end (at VR = 99%). Permeate was withdrawn until the liquid level in the feed tank prevented further concentration.

2.6. Nanofiltration

Around 200 l of the permeate from ultrafiltration was further treated with a NF membrane to produce high-quality fresh water. The flux and retention of four NF membranes have been studied previously when treating process water sequentially by microfiltration, ultrafiltration and nanofiltration (Persson et al., 2009). The NF99HF membrane from Alfa Laval was found to have a significantly higher flux and a higher retention of lignin and charged compounds (measured as conductivity) than the other membranes, and was therefore used in this investigation.

A 2517 NF99HF spiral membrane with a 30 mil (0.8 mm) spacer from Alfa Laval was used. A smaller spacer than in the UF module could be used since the risk of blocking the feed flow channel was markedly reduced after ultrafiltration. The membrane area of the module is 1.1 m^2.

The material in the NF membrane is more temperature sensitive than the material in the UF membrane. Filtration was therefore performed at 50 °C (the maximum recommended temperature for the membrane). The transmembrane pressure was 20 bar and the cross-flow was 1.1 m^3/h.

2.7. Analyses

2.7.1. Total solids, suspended and dissolved matter, and ash

Samples were dried in weighed aluminium dishes at 105 °C to constant weight. The total solids (TS) content was then calculated by weighing of the residue.

Samples were filtered through a weighed glass fibre filter (Whatman GFB) with pore size 1.0 μm. The MF retentate samples were diluted before filtration, since filtration of the undiluted samples was very difficult. The filtrate and the filter with the resulting filter cake were dried in separate dishes at 105 °C to constant weight. The content of suspended matter was then calculated after weighing the filter cake. The content of dissolved matter was calculated after weighing the filtrate. Thus, the suspended matter is defined as the solid material retained by a filter with 1 μm pores and the dissolved matter as compounds that pass through the filter.

Samples were heated to 575 °C, and this temperature was maintained for 24 h. The samples were then kept at 105 °C for a minimum of 4 h. The ash content was determined by weighing the sample.

2.7.2. Lignin

The lignin content was determined by measuring the light absorption at a wavelength of 280 nm, using a Shimadzu UV-160 spectrophotometer (Kyoto, Japan) and an extinction coefficient of 17.8 l/(g cm) (Örså et al., 1997). Before measurement, the samples were filtered through a glass fibre filter (pore size 1.0 μm) and diluted with deionized water. It must be pointed out that other materials in the samples, for example, extractives and carbohydrate-derived compounds, also absorb UV light at 280 nm (Song et al., 2008). This may lead to overestimation of the lignin concentration.

2.7.3. Hemicelluloses and monosaccharides

The concentration of hemicelluloses was determined after hydrolysing the polysaccharides to monomeric sugars by acid hydrolysis, according to the standardized NREL method (Ruiz and Ehrman, 1996). Before hydrolysing the samples, they were filtered through a glass fibre filter (pore size 1.0 μm). The concentration of monomeric sugars was then analysed using high-performance anion-exchange chromatography and a pulsed amperometric ED40 electrochemical detector (Dionex, CA, USA). The chromatograph was equipped with a GP40 gradient pump, an AS50 autosampler

Table 1
Results from the experiments (the streams are denoted as in Fig. 2).

	In	Permeate				Retentate			
Stream	1	2	3	4	5[a]	R1	R2	R3	R4[a]
Total solids (wt.%)	0.51	0.43	0.40	0.29	0.03	2.10	2.52	10.96	0.49
Suspended matter (g/l)	0.90	0.09	–	–	–	12.64	3.22	–	–
Lignin (g/l)	0.73	0.72	0.72	0.61	0.02	0.62	3.85	14.20	1.14
Hemicelluloses (g/l)	1.15	1.16	0.83	0.07	–	1.31	11.55	64.18	–
Monosaccharides (g/l)	–	–	0.04	0.04	n.d.	–	–	–	–
Conductivity (mS/cm)	2.0	–	2.1	2.0	0.2	–	–	4.5	3.3
Ash (g/l)	1.76	–	1.76	1.70	n.d.	1.93	1.79	7.81	3.03
Al (mg/l)	1.49	–	–	1.37	0.03	–	–	–	
Ca (mg/l)	37.2	–	–	32.2	0.6	–	–	–	
Fe (mg/l)	1.23	–	–	2.22	0.04	–	–	–	
Cl (mg/l)	15.8	–	–	14.2	7.2	–	–	–	
SO_4–S (mg/l)	275	–	–	312	15	–	–	–	
Purity[b] (%)	28	28	21	–	–	16	52	60	

n.d. = Not detectable with amount of sample available.
– = Not analysed.

[a] At VR = 50%.

[b] Hemicellulose concentration/dissolved matter.

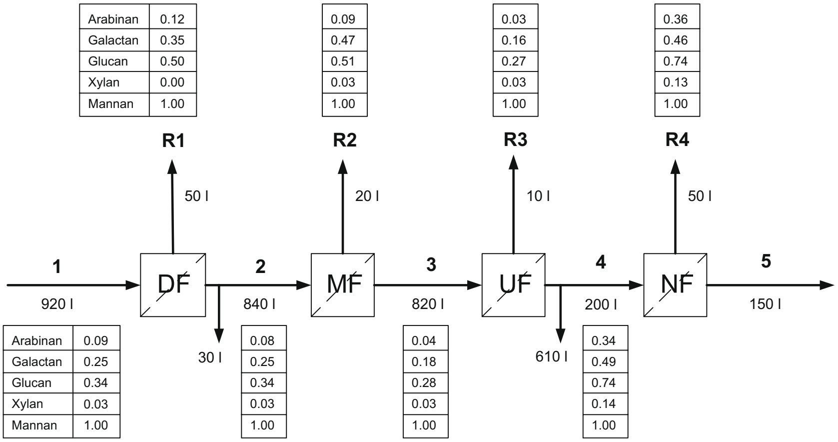

Fig. 2. Water flows in the process stages and relative amount of saccharides in the various streams of the fractionation process. Stream 1 is the process water, stream 5 the purified fresh water (NF permeate) and R denotes retentate streams. The total process time was 48:1 h in the DF stage, 23 h in the MF stage, 20 h in the UF stage and 4 h in the NF stage.

and a Carbo Pac PA10 column (all from Dionex). The injection volume was 10 µl, and deionized water with 2 mM NaOH was used as eluent, at a flow rate of 1 ml/min. D-Mannose, D-glucose, D-galactose, D-xylose and L-arabinose (Fluka Chemie AG, Switzerland) were used as standards.

Monomeric sugars were analysed before and after acid hydrolysis and the oligo- and polysaccharide content was calculated from the difference in monosaccharide concentration before and after hydrolysis. Anhydro corrections of 0.9 and 0.88 were used for the hexoses and pentoses, respectively.

2.7.4. Inorganic ions

The concentration of inorganic cations was determined by inductively coupled plasma atomic emission spectroscopy (ICP AES) with a Perkin–Elmer (MA, USA) Optima 3000DV ICP AES instrument. The concentration of inorganic anions was determined by ion chromatography with an ion chromatograph, model 861 Advanced IC (Metrohm, Switzerland) equipped with a Metrosep A Supp column.

2.7.5. Extractives

The content of extractives was determined by gas chromatography (GC) after acid hydrolysis according to the standardized method SCAN-W 151 XE of the Nordic Standardization Programme, NSP (SCAN). The analysis was performed using an Agilent Technologies GC 6890 N gas chromatograph.

3. Results and discussion

The process water was successfully fractionated using the process described above. The water flows in each process stage are shown in Fig. 2. Around 30 l of the filtrate from the drum filtration was rinsed away, since we had no effective way of removing the last of the filtrate from the drum filter. Only part of the UF permeate was used in the nanofiltration stage (200 l). The results from the experiments are given in Table 1.

3.1. Fractionation of substances

Five fractions were obtained in the process. Four streams containing purified and concentrated substances (R1, R2, R3 and R4) and a purified water stream (stream 5). The major part of the suspended matter was recovered in stream R1 during drum filtration, about 60% of the hemicelluloses in stream R3 during ultrafiltration, and most of the lignin and salts in stream R4 during nanofiltration (see Table 2).

Mass balances for TS, hemicelluloses and lignin over each stage showed differences between the ingoing and outgoing mass of less than 10% for all stages except in the NF stage, which indicates that the results are reliable. Low concentrations in the streams in the NF stage made the analysis of TS, hemicelluloses, lignin and ash difficult, since large volumes of sample were needed to obtain a reliable result, and only limited amounts of the samples were available.

The concentration of extractives was measured in the process water, DF filtrate and MF permeate. The drum filter retains some of the extractives since the concentration in the drum filter filtrate is about 20% lower than the concentration in the process water. The MF permeate only contained a few percent of the ingoing concentration (see Table 3), indicating that the remaining extractives are almost totally retained by the microfiltration membrane. Thus, stream R2 contains most of the extractives.

Table 2
Recovery as a percentage of the content of the substance in the process water.

Substance/stream	DF retentate R1 (%)	MF retentate R2 (%)	UF retentate R3 (%)	NF retentate R4 (%)
Suspended matter	76	8	4	0
Hemicelluloses	6	23	63	0
Lignin	5	12	22	72
Ash	6	2	5	79

Table 3
Concentration of extractives in the process water, the filtrate from the drum filter and the MF permeate.

	Process water (stream 1)	DF filtrate (stream 2)	MF permeate (stream 3)
Saturated fatty acids (mg/l)	5	4	0.4
Unsaturated fatty acids (mg/l)	31	25	0.4
Sterols (mg/l)	8	6	0.1
Resin acids (mg/l)	8	6	0.4
Total (mg/l)	52	41	1.3

3.2. Composition of different fractions

The yield of a substance depends not only on the volume reduction and the retention of this substance in the specific process stage, but also on the retention and VR in previous stages. Less hemicelluloses would have been recovered in the MF retentate (stream R2) if the VR had been higher in the MF stage, for example. Retention and volume reduction also have considerable impact on the purity of a fraction. The lignin/hemicellulose ratio in the UF retentate (stream R3), for example, was 0.56 at VR = 50%, 0.29 at VR = 90% and 0.22 at VR = 99%.

The composition of the process water and the concentrated fractions is shown in Fig. 3. Suspended matter is the major component in the drum filter retentate, hemicelluloses in the MF and UF retentates, and inorganic substances (ash) in the NF retentate.

3.2.1. Drum filtration

Hemicelluloses, lignin and ash were not retained during drum filtration. The recovery of these substance in the DF retentate is therefore only due to the VR in this stage. The volume reduction during drum filtration was 95%, which means that 95% of hemicelluloses, lignin and ash were recovered in the DF filtrate. The DF retentate has a high content of suspended matter, as shown in Fig. 3, making it interesting for recycling to the pulping process if the concentration of extractives is sufficiently low. Further investigations of this fraction would thus be interesting.

3.2.2. Microfiltration

An appreciable amount of hemicelluloses was retained during MF, which made hemicelluloses the major component in the MF retentate. Nonetheless, about 75% of the hemicelluloses and 90% of the lignin in the feed were recovered in the MF permeate. These values would have been even higher if a higher VR had been used.

3.2.3. Ultrafiltration

About 95% of the hemicelluloses but only 25% of the lignin in the feed were recovered in the UF retentate, which means that hemicelluloses were not only concentrated (final concentration 64 g/l), but also purified, as shown in Fig. 3. Besides a significant amount of lignin, also low-molar-mass substances, such as monosaccharides and inorganic ions, were removed.

The amount of hemicelluloses in the UF retentate in relation to the dissolved matter was 60%. Higher purities have been reported in previous investigations of the isolation of GGM from TMP process water. However, in these cases additional purification stages after ultrafiltration were used. Hartman et al. (2006b) obtained a purity of GGM of about 90% after ultrafiltration with a 1 kDa membrane and diafiltration of the UF retentate. Among the impurities, lignin was the most abundant. Willför et al. (2008) report 70–80 mol.% purity of GGM recovered from process water in two Finnish TMP mills using a combination of different filtration and ultrafiltration stages followed by spray drying or precipitation in ethanol. The main impurities were arabinogalactans and pectic acids. Willför et al. (2008) made attempts to further purify the GGM, but this proved to be difficult without losses in yield or solubility (due to deacetylation). They concluded that obtaining truly pure GGM, without any aromatic structures or other sugars attached to the backbone, would be extremely difficult.

3.2.4. Nanofiltration

The purpose of the nanofiltration stage is to act as a kind of kidney, rejecting matter that accumulates in pulp mills with closed process stream recirculation systems. The quality of permeate to be reused in the mill depends to a large extent on where in the process it is to be used. However, carbohydrates are preferentially removed as paper mill bacteria thrive on low-molar-mass carbohydrates (Willför et al., 2003a). Reducing the content of inorganic elements reduces the risk of scaling problems in the mill.

The major components in the NF retentate were salt, carbohydrates and lignin (or other aromatic compounds detected as lignin). The carbohydrates were efficiently retained by the NF membrane, and the concentration of inorganic elements was also markedly lower in the NF permeate than in the process water. The conductivity was 1/10 and the concentrations of calcium, aluminium and iron were about 1/60, 1/50 and 1/30, for example.

3.3. Composition of carbohydrates in all streams

The composition of the carbohydrate content in the various streams differs, as shown in Fig. 2, although it is similar in the process water (stream 1), the DF filtrate (stream 2) and the MF permeate (stream 3). The DF retentate (stream R1), the MF retentate (stream R2) and the UF permeate (stream 4) contain higher amounts of galactan and glucan than the other streams. The relative amount of all saccharides, except mannan, is higher in the UF permeate, because GGM are preferentially retained in the UF stage.

Willför et al. (2003b) showed that mainly GGM are released from both wood and pulp, but also a surprisingly large amount of arabinans, originating from arabinogalactan, and minor amounts of pectins and xylans. Variations in sugar content composition are therefore presumably due to varying degrees of retention of GGM and, for example, arabinogalactan, in each process stage. The saccharide composition of the process water was 59% mannan, 20% glucan, 14% galactan, 5% arabinan and 2% xylan. The corresponding values for the UF retentate were 68% mannan, 18% glucan, 11% galactan, 2% arabinan and 0% xylan. The ratio Man/Glc/Gal was 3.7:1:0.6 in the UF retentate, which is similar to the results of Willför et al. (2003b, 2008).

3.4. Performance of each process stage

3.4.1. Drum filtration

The objective of the drum filtration stage is to remove particles and fines that would otherwise block the flow channels in the membrane elements in the subsequent process stages. The content of suspended matter was effectively lowered. Only 10% of the suspended matter remained in the filtrate (stream 2).

The maximum filtration flow was measured and found to be about 31 l/min. As the concentration of solids in the concentrate increased, the filtration flow decreased. A mean value of 29 l/min was calculated, which corresponds to approximately 2 m^3/m^2 h.

3.4.2. Microfiltration

The spiral-wound membranes used in the ultrafiltration stage are susceptible to blocking by particles and suspended matter. Prefiltration of the feed down to 25–50 μm is recommended for a 45-mil spacer channel (Cheryan, 1998). The aim of the microfiltration

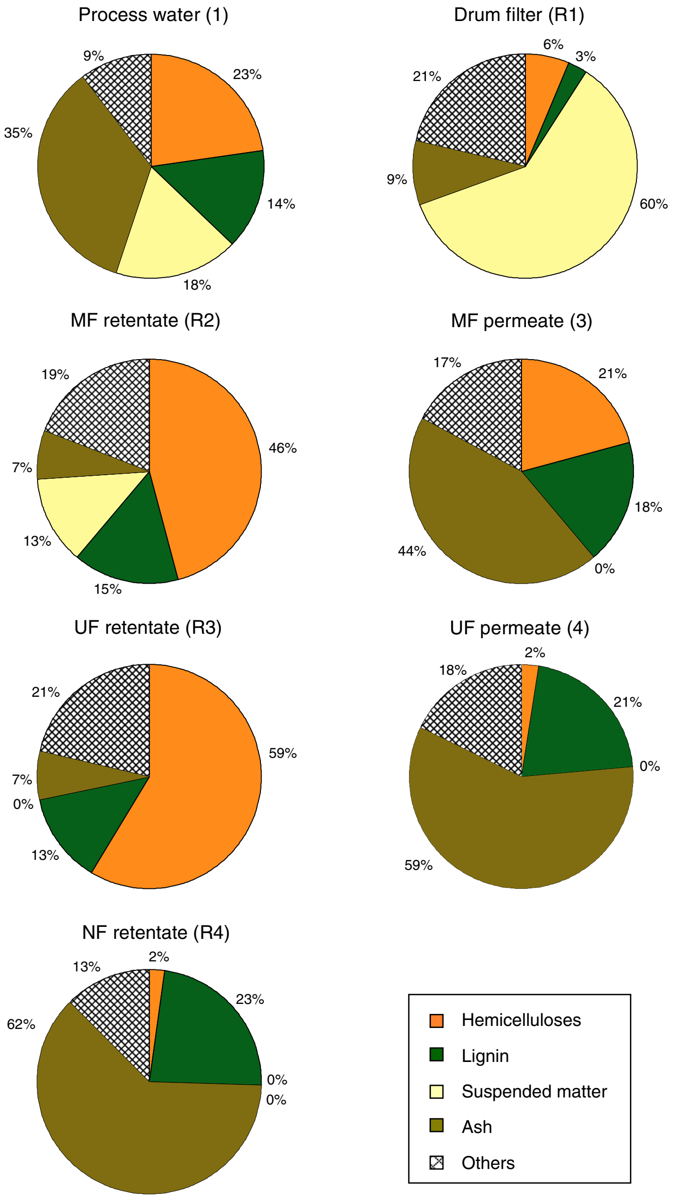

Fig. 3. Composition of total solids content in the streams from the four process stages. The compounds (clockwise) are: hemicelluloses (monosaccharides in case of the NF retentate), lignin (measured as UV absorbance at 280 nm), suspended matter, salt (measured as ash) and other, non-identified compounds.

stage was thus to produce a permeate suitable as the feed to spiral-wound modules and, at the same time, isolate the extractives in the retentate.

The flux was high and relatively stable during semi-batch operation mode, and decreased rapidly during batch concentration, as shown in Fig. 4a. The average flux during semi-batch operation was 330 l/m^2 h and for the total process 300 l/m^2 h.

The relatively stable flux during semi-batch operation indicates that no significant fouling took place. Furthermore, the flux was successfully recovered after cleaning.

MF was stopped at a volume recovery of 98%, since the volume in the feed tank was too small to keep the temperature constant at this point. An even higher VR could have been achieved if the initial volume had been bigger since the flux was still high when filtration was discontinued.

A high concentration of hemicelluloses in the feed solution to the ultrafiltration stage (stream 3) is beneficial, as a smaller amount of water needs to be removed to reach the predetermined concentration of hemicelluloses in the final product. Low retention of hemicelluloses during microfiltration is thus advantageous. However, the retention was rather high. The initial retention was 55% and the final retention 90%. The high retention of hemicelluloses during microfiltration leads to a decrease in concentration from 1.2 g/l in the feed solution to 0.8 g/l in the permeate. Increasing the VR would increase the concentration of hemicelluloses in the permeate, as shown in Fig. 4b.

The high retention of hemicelluloses is unexpected as hemicelluloses are normally small enough to pass through MF membranes. The reason may be that the hemicelluloses are bound to the solid material or entrapped in the filter cake formed by retained solids on the membrane. The hypothesis about adsorption is strengthen by the observation by Willför et al. (2003a) that GGM can act as emulsion stabilizers of pitch droplets and that arabinan can be linked to lignin in lignin–carbohydrate complexes (Willför et al., 2003b).

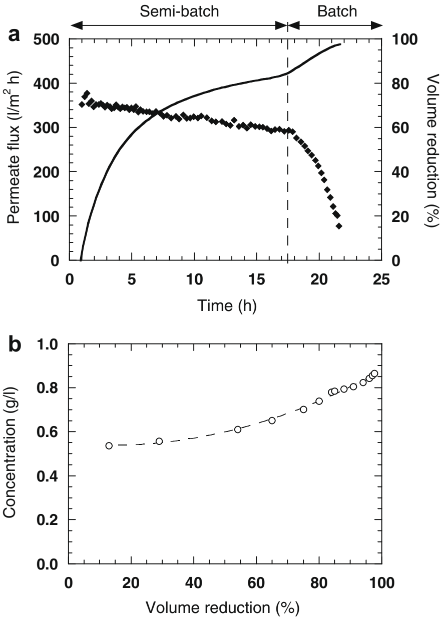

Fig. 4. (a) Permeate flux (♦) and volume reduction (—) during microfiltration. (b) Concentration of hemicelluloses in the total permeate (○) as a function of volume reduction during microfiltration.

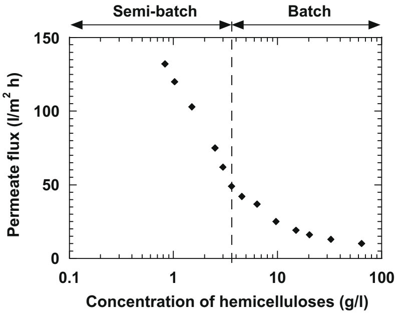

Fig. 5. Permeate flux as a function of hemicellulose concentration during ultrafiltration.

3.4.3. Ultrafiltration

The aim of the ultrafiltration stage is to concentrate and purify GGM. A high concentration of hemicelluloses (64 g/l) was obtained. However, due to the low concentration in the feed, a high volume reduction (99%) was needed to achieve this concentration. The retention was high and increased during concentration (from 93% to 99%).

The relative amount of hemicelluloses was much higher in the UF retentate (stream R3) than in the process water, as shown in Fig. 3. Salt was the major substance in the UF permeate (4). Hemicelluloses only represent a minor amount of the total solids content of this stream. Suspended matter and extractives are removed in the first two stages (drum filtration and microfiltration), and were thus not present in the following streams (i.e., stream 3, 4, etc.).

The flux as a function of hemicellulose concentration is shown in Fig. 5. The initial content of hemicelluloses was 0.8 g/l, 3.6 g/l at the end of semi-batch operation (VR = 80%), 9.7 g/l at VR = 95% and 64.2 g/l at the end of the run (VR = 99%). The classical gel model (which predicts a linear relationship between flux and log concentration) cannot be directly applied in this case. The flux decrease levels off with increasing concentration, as can be seen in the figure. This could be due to changes in fouling when switching from semi-batch to batch mode.

The flux decreased drastically during the experiment, as can be seen in Fig. 6a. The mean flux observed to achieve a hemicellulose concentration of 33 g/l was 60 l/m^2 h, and a flux of 58 l/m^2 h was measured to reach 64 g/l. The flux decrease during semi-batch operation is in marked contrast to the stable flux during microfiltration. This flux decrease seems to be due to fouling and not to an increase in concentration, since the concentration did not increase drastically until after VR ~ 95%. The pure water flux could not be recovered by cleaning after the experimental run using the alkaline cleaning agent Ultrasil 10 or the acidic cleaning agent Ultrasil 70 (Henkel Chemicals Ltd., Germany). Cleaning with Ultrasil 10 was successful in a previous study (Persson, 2009). However, the final volume reduction was higher in this study and severe fouling was observed at the end of the volume reduction. It is well

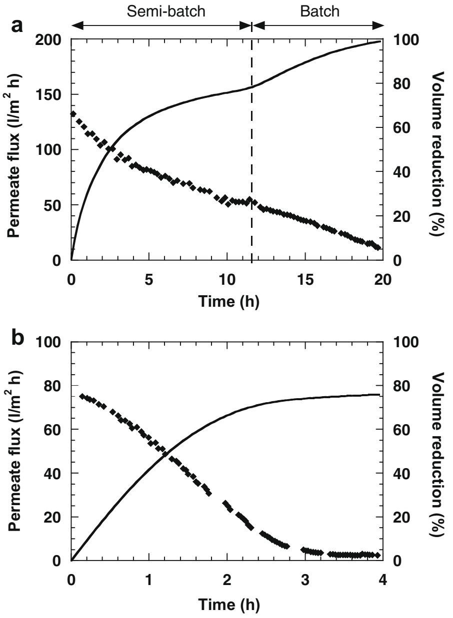

Fig. 6. Permeate flux (♦) and volume reduction (—) as a function of time during (a) ultrafiltration and (b) nanofiltration.

known that the degree of fouling and hardship of cleaning are closely related. In a commercial plant cleaning would be initiated when flux had decreased to a certain, predetermined level, thereby avoiding too severe fouling of the membrane.

3.4.4. Nanofiltration

A volume reduction of 76% was achieved. The retention of ions, measured as the conductivity, was 85–94%. The concentration of carbohydrates in the permeate was below the detection limit. The permeate at a VR of 50% was of good quality with low ion concentrations. However, the concentration of ions in the permeate increased significantly at a volume reduction of 76%, as can be seen from Table 4. Furthermore, the concentration of ions in the retentate at a VR of 76% reached levels at which there is a risk of scaling and gypsum formation. The solubility of gypsum is 2.05 g/l (Lide, 2008). The concentration at the membrane surface is markedly higher than in the bulk solution due to concentration polarization and, therefore, it would be wise to not exceed VR 50–60% in an industrial application.

Table 4
Characteristics of the feed, permeates at VR = 50% and 76%, and the retentate at VR = 76%, in the nanofiltration stage. SO_4–S is the concentration of sulphur in the form of sulphate.

	Feed	Permeate at VR = 50%	Permeate at VR = 76%	Retentate at VR = 76%
Lignin (g/l)	0.61	0.03	0.29	2.08
Carbohydrates (g/l)	0.12	n.d.	0.02	0.32
Conductivity (mS/cm)	2.0	0.2	0.7	5.0
Al (mg/l)	1.37	0.03	0.56	4.42
Ca (mg/l)	32.2	0.6	12.4	127.6
Fe (mg/l)	2.22	0.04	0.97	7.09
Cl (mg/l)	14.2	7.2	7.2	28.2
SO_4–S (mg/l)	312	15	152	835

The flux decreased steadily and was very low at the end of the concentration run, as can be seen in Fig. 6b. The average flux until a VR of 50% was reached was 63 l/m^2 h and when a VR of 76% was reached 27 l/m^2 h.

4. Conclusions

It has been shown that process water in thermomechanical pulp mills can be fractionated into several potentially valuable products. In the drum filtration stage, 90% of the suspended solids were removed. In the subsequent MF stage, the remaining solids and the extractives were removed. A concentrated and purified hemicellulose solution was separated in the UF stage. In the NF stage, purified water of fresh water quality could be produced. The proposed method was successfully operated at conditions closely resembling industrial conditions by treating a large volume of process water and running the process stages back-to-back.

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References

Cheryan, M., 1998. Ultrafiltration and Microfiltration Handbook. Technomic Publishing Co., Lancaster, USA.
Eckerman, C., Adams, M., Holmbom, B., Sundberg, K., 2002. Method for Recovering Non-fibrous Substances from Wood Material. Patent Application PCT/WO0240767.
Hansen, N.M.L., Plackett, D., 2008. Sustainable films and coatings from hemicelluloses: a review. Biomacromolecules 9 (6), 1493–1505.
Hartman, J., Albertsson, A.-C., Söderqvist Lindblad, M., Sjöberg, J., 2006a. Oxygen barrier materials from renewable sources: material properties of softwood hemicellulose-based film. J. Appl. Polym. Sci. 100, 2985–2991.
Hartman, J., Albertsson, A.-C., Sjöberg, J., 2006b. Surface- and bulk-modified galactoglucomannan hemicellulose films and film laminates for versatile oxygen barriers. Biomacromolecules 7, 1983–1989.
Lide, D.R. (Ed.), 2008. CRC Handbook of Chemistry and Physics, 89th ed. 2008–2009.
Lundqvist, J., Jacobs, A., Palm, M., Zacchi, G., Dahlman, O., Stålbrand, H., 2003. Characterization of galactoglucomannan extracted from spruce (*Picea abies*) by heat-fractionation at different conditions. Carbohydr. Polym. 51 (2), 203–211.
Mikkonen, K.S., Tenkanen, M., Cooke, P., Xu, C., Rita, H., Willför, S., Holmbom, B., Hicks, K.B., Yadav, M.P., 2009. Mannans as stabilizers of oil-in-water beverage emulsions. LWT – Food Sci. Technol. 42, 849–855.
Örså, F., Holmbom, B., Thornton, J., 1997. Dissolution and dispersion of spruce wood components into hot water. Wood Sci. Technol. 31, 279–290.
Palm, M., Zacchi, G., 2003. Extraction of hemicellulosic oligosaccharides from spruce using microwave oven or steam treatment. Biomacromolecules 4 (3), 617–623.
Palm, M., Zacchi, G., 2004. Separation of hemicellulosic oligomers from steam-treated spruce wood using gel filtration. Sep. Purif. Technol. 36 (3), 191–201.
Persson, T., 2009. Extraction and isolation of hemicelluloses from agricultural and forestry waste streams, PhD thesis, Department of Chemical Engineering, Lund University, Sweden.
Persson, T., Nordin, A.-K., Zacchi, G., Jönsson, A.-S., 2007. Economic evaluation of isolation of hemicelluloses from process streams from thermo-mechanical pulping of spruce. Appl. Biochem. Biotechnol. 136–140, 741–752.
Persson, T., Ren, J.-L., Jönsson, A.-S., 2009. Purification of process water in a thermomechanical pulp mill by nanofiltration. LUTKDH/(TKKA-7001)/1–7/(2009). Department of Chemical Engineering, Lund University.
Ruiz, R., Ehrman, T., 1996. Dilute Acid Hydrolysis Procedure for Determination of Total Sugars in the Liquid Fraction of Process Samples. Laboratory Analytical Procedure-014.
SCAN-W 151 XE of the Nordic Standardization Programme, NSP. <http://innventia.se/templates/STFIPage_7113.aspx>.
Söderqvist Lindblad, M., Ranucci, E., Albertsson, A.-C., 2001. Biodegradable polymers from renewable sources. New hemicellulose-based hydrogels. Macromol. Rapid Commun. 22, 962–967.

Söderqvist Lindblad, M., Albertsson, A.-C., Ranucci, E., Laus, M., Giani, E., 2005. Biodegradable polymers from renewable sources: rheological characterization of hemicellulose-based hydrogels. Biomacromolecules 6, 684–690.

Song, T., Pranovich, A., Sumerskiy, I., Holmbom, B., 2008. Extraction of galactoglucomannan from spruce wood with pressurised hot water. Holzforschung 62, 659–666.

Sundholm, J. (Ed.), 1999. Mechanical Pulping, Papermaking Science and Technology Series, vol. 5. Finnish Paper Engineers' Association and TAPPI, Gummers Printing, Jyväskylä, Finland.

Thornton, J., Ekman, R., Holmbom, B., Örså, F., 1994. Polysaccharides dissolved from Norway spruce in thermomechanical pulping and peroxide bleaching. J. Wood Chem. Technol. 14 (2), 159–175.

Willför, S., Rehn, P., Sundberg, A., Sundberg, K., Holmbom, B., 2003a. Recovery of water-soluble acetyl-galactoglucomannans from mechanical pulp of spruce. Tappi J. 2 (11), 27–32.

Willför, S., Sjöholm, R., Laine, C., Roslund, M., Hemming, J., Holmbom, B., 2003b. Characterisation of water soluble galactoglucomannans from Norway spruce wood and thermomechanical pulp. Carbohydr. Polym. 52, 175–187.

Willför, S., Sundberg, K., Tenkanen, M., Holmbom, B., 2008. Spruce-derived mannans – a potential raw material for hydrocolloids and novel advance natural materials. Carbohydr. Polym. 72, 197–210.

Xu, C., Willför, S., Holmlund, P., Holmbom, B., 2009. Rheological properties of water-soluble spruce *O*-acetyl galactoglucomannans. Carbohydr. Polym. 75, 498–504.

Paper II

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Separation of dispersed substances and galactoglucomannan in thermomechanical pulp process water by microfiltration

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ABSTRACT

Several valuable substances are released from wood during the production of thermomechanical pulp. These substances can be isolated and purified for use as value-added chemicals. The hemicellulose galactoglucomannan (GGM) has attracted a great deal of interest because of its possible applications as an oxygen barrier film in packaging materials, as a hydrogel in biomedical products and as an emulsion stabilizer in food and feed. In order to exploit GGM in pulp mill process water, it must be recovered at a high concentration and high purity. The first step in the purification process is the separation of GGM and dispersed substances. In this work, the influence of membrane pore size, cross-flow velocity and backpulsing on membrane performance during the microfiltration of thermomechanical pulp process water was investigated. The flux of 0.4 and 0.8 μm membranes was lower than the flux of a 0.2 μm membrane, and it was not possible to recover the pure water flux of the 0.4 and 0.8 μm membranes. Increased cross-flow velocity and backpulsing had a positive effect on the flux, but only a minor influence on the retention. The mean molecular mass of GGM in the process water was 9 kg/mol. The retention was therefore expected to be <10%. However, the retention of GGM was >50%, irrespective of the operating conditions.

1. Introduction

Various substances are released and dissolved in the process streams during the production of thermomechanical pulp (TMP). Much of the material released ends up in the waste water, leading to costly treatment. The removal of substances in the process water will reduce the load on the waste water treatment plant thereby reducing this cost. At the same time, the recovered substances can be utilized as renewable sources of, for example, specialty chemicals and biofuels. In this connection, hemicelluloses have attracted much interest [1–6]. Galactoglucomannan (GGM) is the main hemicellulose in Norway spruce (*Picea abies*), the most common raw material used in TMP mills in the Nordic countries.

Several processes for the removal and separation of dispersed and dissolved substances in TMP process water have been presented. In a patent published in 2002 Sundberg et al. [7] describe a method for recovering non-fibrous substances including wood resins, water soluble aromatic compounds, salts and GGM from wood material being processed in a mechanical pulping process. Their method consists of four stages and is applicable on different process streams including TMP process water. Fibers and larger particles are first removed by pressing or filtration. Filtration, flotation, centrifugation or extraction is suggested in a second stage to separate non-soluble colloidal wood resins. Aromatic compounds may be separated in a third stage utilizing adsorbents, aromatic exchange resin, chromatography or membrane filtration processes. Finally dialysis or reverse osmosis is suggested in order to separate salts and GGM. Willför et al. [8] used one type of this method in a recent study, in which they recovered GGM from mechanical pulp at a yield of 5 kg/ton pulp and a purity of 95%. Colloidal material, primarily resins and microfines, were removed after aggregation with a cationic polymer. Aromatic substances were adsorbed onto a polyacrylate resin, and GGM was concentrated and purified by ultrafiltration (UF), with possible further purification by precipitation in ethanol. Persson et al. [9] have presented a method based entirely on filtration and membrane filtration. In this process, dispersed substances and colloidal material, primarily resins, are removed by drum filtration (DF) and microfiltration (MF). GGM is concentrated and separated from aromatic substances, primarily lignin, by UF. Finally, lignin is recovered by nanofiltration.

A common observed problem in the methods presented above is the loss of desired products such as GGM during processing. Willför et al. [8] report in their study a loss of GGM of about 30% when using aggregation and adsorption before GGM recovery. The alternative use of microflotation suggested by Sundberg et al. [7] was also found to be accompanied with substantial GGM losses and had furthermore an undesired low efficiency of removing colloidal wood resins [8]. Persson et al. [9] observed an unexpectedly

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high amount of GGM to be removed together with the dispersed substances during the MF stage in their method.

Previous work done in this field show that several promising methods to recover valuable substances in TMP process water exist. Furthermore, the various substances found in TMP process water have been extensively studied [10–17] providing the basic information on their properties required for a successful separation. However, we still lack information on how these existing methods should be operated in the most optimal way in order to reduce losses during processing. This work is focused on the use of MF as a potential method for separation of dispersed substances and GGM. Even though Persson et al. [9] used MF in their work for this purpose, so far no study has been presented in which this method has been investigated in detail on TMP process water. The aim of this work was to evaluate the MF technique and determine suitable operation conditions to realize highest possible recovery of GGM in the MF permeate. Several operating conditions including the use of backpulsing were studied in this work.

2. Theory

The observed retention of a membrane is defined as:

$$R_{obs} = 1 - \frac{C_p}{C_b} \tag{1}$$

where C_p and C_b are the concentrations in the permeate and the bulk of the feed. If a sieving mechanism is assumed to be the prevalent retention mechanism, the true retention is given by:

$$R_{true} = 1 - \frac{C_p}{C_m} = 1 - \left(1 - \frac{d_h}{d_p}\right)^2 \tag{2}$$

where C_m is the concentration at the membrane surface on the feed side of the membrane, d_h is the hydrodynamic diameter of the substance and d_p the pore diameter. The diameter of a rigid spherical substances is given by:

$$d = \left(\frac{6M_s}{N_A \pi \rho_s}\right)^{1/3} \tag{3}$$

where M_s is the molecular mass of the substance, N_A is Avogadro's number, and ρ_s the density of the substance (often approximated by the density of water).

The intrinsic viscosity $[\eta]$ can be used to calculate the hydrodynamic volume of the solute from the molecular mass as $([\eta]\cdot M_s)$ is proportional to the hydrodynamic volume of the solute. Meireles et al. [18] used this relation to estimate the sieving coefficients of UF and MF membranes. The intrinsic viscosity of polyethylene glycol (PEG) was calculated using the empirical correlation:

$$[\eta] = 4.9 \cdot 10^{-2} \cdot (1000 \cdot M_s)^{0.672} \tag{4}$$

Hence, the hydrodynamic diameter of PEG, used for calibration during size-exclusion chromatography (SEC) in this study, is given by:

$$d_h = \left(4.9 \cdot 10^{-2} \cdot (1000 \cdot M_s)^{0.672} \cdot \frac{6M_s}{N_A \pi \rho_s}\right)^{1/3} \tag{5}$$

The hydrodynamic volume, rather than the molecular mass, determines the separation during SEC. It is therefore relevant to use the hydrodynamic diameter of PEG to calculate the size of GGM, when calculating the true retention during MF.

3. Materials and methods

3.1. Raw material

The process water used in the investigation was withdrawn from the disc filters after the refiners at a TMP mill located in central Sweden. In the pulp mill this stream is recirculated before discharging it into the sewage system. The pulp mill uses softwood (mainly spruce) as raw material. Process water was withdrawn on seven occasions over a period of one year. About 1 m^3 of process water was withdrawn on each sampling occasion, and immediately transported to our department. The temperature of the process water at the mill is 80 °C and the pH about 4.2.

3.2. Pretreatment

Directly after receiving the process water from the pulp mill, coarse material that would block the feed channels in the MF membrane modules was removed, either using DF or a 1 mm mesh. The filtration area of the drum filter (HDF802-1F, Hydrotech AB, Vellinge, Sweden) was 0.9 m^2. The most dense filter cloth available, with a pore size of 10 μm, was used. During DF the solid material formed a filter cake on the filter cloth. This solid material was removed from the cloth by spraying filtrate onto the reverse side. The concentrate stream was recycled to the feed tank, while the filtrate was continuously withdrawn and subsequently treated by MF.

3.3. Microfiltration

MF was performed in two bench-scale units equipped with tubular ceramic membranes made of alumina oxide (Atech Innovations GmbH, Gladbeck, Germany). Unit I was equipped with a single-feed-channel, 0.2 μm membrane with an area of 0.0047 m^2 (length 0.25 m) and Unit II with a 7-channel membrane element with an area of 0.13 m^2 (length 1.0 m). Membrane elements with pore sizes of 0.2, 0.4 and 0.8 μm were used in this unit. The diameter of the feed channels of all the membranes was 6 mm. Both retentate and permeate were recirculated to the feed tank in all experiments to maintain a constant concentration during the experiment. All data from the instruments were recorded in a computer using LabView software (National Instruments Corp., Austin, TX).

Unit I was equipped with a 5 l feed tank and a magnetic gear pump (MDG-M4T68220H, Iwaki Co. Ltd., Tokyo, Japan). The pressure drop along the feed channel in the membrane can be neglected as the length of the membrane was so short. Pressure was therefore only measured at the outlet of the membrane and on the permeate side, using Jumo 4 AP-30-020/064 pressure transmitters (Jumo AB, Helsingborg, Sweden). A valve on the permeate side was used to regulate the transmembrane pressure. The feed flow was measured with a rotameter and the permeate flow was measured with a PhaseSep flow meter (Phase Separations Ltd., Queensferry, UK). The temperature in the feed tank was measured with a Pt100 element. The retention of GGM in process water, with and without pH adjustment, the retention of GGM in DF filtrate, and the retention of PEG with different molecular masses was studied in Unit I. The pH of the process water was adjusted using sodium hydroxide solution (NaOH 50 wt%, Merck KGaA, Darmstadt, Germany). The NaOH addition was very small compared to the total feed volume, so that dilution due to pH adjustment could be neglected. Experiments with 5 g/l PEG in deionized water were performed at 50 °C, since PEG melts at temperatures above 53 °C, according to the manufacturer.

Unit II was equipped with a backpulse device, as illustrated in Fig. 1. A 200 l feed tank, equipped with an electric heater, was connected via two frequency-regulated pumps to a M1 membrane

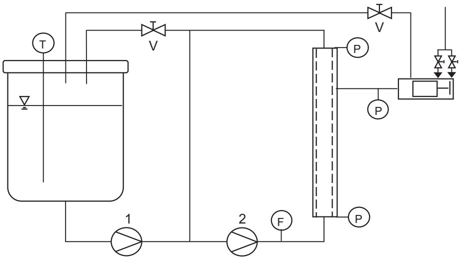

Fig. 1. Schematic illustration of Unit II. *V* are valves used to adjust the transmembrane pressure on the retentate and permeate side, respectively, P: pressure transmitters, F: flow indicator, T: temperature indicator, 1: feed pump and 2: circulation pump.

module (Atech). The first pump (H/G-25-X, Wanner Engineering Inc., Minneapolis, MN) was used as the feed pump, and the second pump (NB32/25-20, ABS Pump Production, Mölndal, Sweden) as a circulation pump. A backpulse device (BF100, Pall Corp., Port Washington, NY) was connected to the permeate port of the M1 module. This device uses an air-driven piston to provide rapid backpulsing. Pressure transmitters (dTrans p02, JumoAB) were installed at the inlet and outlet of the membrane module and on the permeate side. The feed flow was measured with a volume flow meter (Fischer&Porter Co. Ltd., Göttingen, Germany), and the permeate flow was measured gravimetrically with a balance. The temperature in the feed tank was measured with a Pt100 element.

The transmembrane pressure was calculated from the relation:

$$P_t = \frac{P_{in} + P_{out}}{2} - P_p \qquad (6)$$

where P_{in} and P_{out} are the pressures at the inlet and outlet of the membrane module, and P_p is the pressure on the permeate side of the membrane. The transmembrane pressure was varied by regulating the speed of the circulation pump and adjusting the valves (see Fig. 1).

The influence of pore size, cross-flow velocity and backpulsing was studied in Unit II. The performance of membranes with pore sizes of 0.2, 0.4 and 0.8 μm was investigated. The influence of cross-flow velocity during MF with a 0.2 μm membrane was studied at 3 and 5 m/s. The forward filtration time (the time between two backpulses) and the backpulse duration were varied according to the scheme in Table 1 when studying the influence of backpulsing. The backpulsing experiments were performed at 80 °C and 1.1 bar. The reinjection volume per backpulse was 0.1 l and the backpressure in the backpulse device was 9 bar. The flux and retention without backpulsing were used to calculate normalized values of flux and retention during backpulsing.

The same starting procedure was used for all experiments performed in Unit II. The membrane was cleaned before and after filtration of process water by circulating a solution of the alkaline cleaning agent Ultrasil 10 (Ecolab AB, Älvsjö, Sweden) at a concentration of 0.5 wt% and a temperature of 50 °C for 60 min. After cleaning, the system was rinsed thoroughly with deionized water. About 170 l of pretreated TMP process water was circulated in the system at the cross-flow velocity used in the specific experiment. The permeate valve was closed during heating of the process water to the operating temperature. The permeate valve was then opened and the transmembrane pressure adjusted. Flux was recorded for 30 min (cross-flow velocity and backpulsing experiments) or 60 min (pore size experiments) before samples of retentate and permeate were withdrawn.

Table 1
Parametric values used in the backpulsing study.

Cross-flow velocity (m/s)	Forward filtration time (s)	Backpulse duration (s)
5	1	0.25, 0.35
	2	0.25, 0.35
	5	0.25, 0.35
	Without backpulsing	
3	1	0.25, 0.35
	2	0.25, 0.35
	5	0.25, 0.35
	Without backpulsing	

The same starting and cleaning procedure was used in Unit I.

3.4. *Analysis*

The concentrations of total solids and ash were determined according to standardized NREL methods [19,20]. To determine the concentration of suspended solids (SS), a sample of known volume was filtered through a weighed 1.0 μm glass fiber filter (Grade GF/B, Whatman Int. Ltd., Maidstone, UK). The filter was dried to constant weight at 105 °C, and the mass of the filter cake was determined. The concentration of SS was then calculated as the mass of the filter cake divided by the sample volume.

The size distribution of particles in the process water was measured by laser diffraction with a HELOS/LA system (Sympatec GmbH, Clausthal-Zellerfeld, Germany). The system uses a HeNe laser with a wavelength of 632.8 nm for the illumination of the particles. A Fourier lens directs the diffracted light onto a multi-element photodetector, which measures the intensity and distribution of the light. The intensity of the light is converted into an electrical signal and a computer program converts the data into a particle size distribution. The system is capable of detecting particles in the size range 0.9–875 μm.

SEC was used to determine the molecular mass distribution of polysaccharides, GGM and lignin. A liquid chromatography system (Waters 600E, Waters Corp., Milford, MA) was used, consisting of an autosampler (model 717plus, Waters), a column, an absorbance detector (model 486, Waters) and a refractive index (RI) detector (model 410, Waters). Absorbance was measured at a wavelength of 280 nm. The column was packed with 30 cm of Superdex 30 and 30 cm of Superdex 200 (GE Healthcare, Uppsala, Sweden). Samples containing particles were filtered through a 1.0 μm glass fiber filter prior to injection into the column. The injection volume was 1500 μl. As eluent, a 125 mM sodium hydroxide solution was used at a flow rate of 1 ml/min. The system was calibrated with PEG standards having peak molecular masses of 0.4, 4, 10 (Merck Schuchardt OHG, Hohenbrunn, Germany) and 40 kg/mol (Serva Electrophoresis GmbH, Heidelberg, Germany). The mean molecular mass distribution was determined by collecting nine fractions, for a period of 10 min each, starting at an elution time of 29 min and ending at 119 min, and analyzing the concentration of polysaccharides and lignin in each fraction.

The concentration of polysaccharides was determined by first hydrolyzing the polymers to monomeric sugars and then analyzing the monosaccharide concentration using high-performance anion-exchange chromatography coupled with pulsed amperometric detection. Acid hydrolysis was performed according to the standardized NREL method [21]. An ion chromatography system (ICS-3000, Dionex Corp., Sunnyvale, CA), equipped with a Carbo Pac PA 1 analytical column and an ED40 electrochemical detector, was used to determine the monosaccharide concentration. A solution of 200 mM sodium hydroxide dissolved in 170 mM sodium acetate was used to clean the column. Deionized water was used as eluent at a flow rate of 1 ml/min. The sample injection volume was 10 μl. The monomeric sugars D-glucose, D-galactose, D-mannose,

Table 2
Concentration of substances in TMP process water withdrawn after the refiner.

	TS	SS	PS	Lignin	Ash	Resins
Concentration (g/l)	5.6 ± 0.5	1.16 ± 0.5	1.33 ± 0.03	0.86 ± 0.03	1.96 ± 0.2	0.051 ± 0.0004
Number of batches analyzed	2	6	7	6	2	2

TS = total solids, SS = suspended solids, PS = polysaccharides.

D-xylose, and L-arabinose (Fluka Chemie AG, Buchs, Switzerland) were used as standards.

Absorbance was measured at a wavelength of 280 nm with a spectrophotometer (UV-160, Shimadzu Corp., Kyoto, Japan). The apparent concentration of lignin was calculated from the absorbance using an extinction coefficient of 17.8 l/(g cm) [11]. Samples containing particulate material were filtered through a 1.0 μm glass fiber filter before the measurements.

The concentration of wood resins was determined using a standardized method (SCAN-W 151 XE, method A) of the Nordic Standardization Programme [22]. A gas chromatograph (GC 6890 N, Agilent Technologies, Santa Clara, CA) was used for identification and quantification of the wood resins.

The concentration of PEG was determined by measuring the chemical oxygen demand (COD) with a COD cuvette test (LCK 114) and an ISIS 9000 MDA photometer (Hach Lange GmbH, Düsseldorf, Germany). The concentrations were used to calculate the observed retention of PEG using Eq. (1).

4. Results and discussion

4.1. Composition of the process water

The total solids content of the process water was rather low, only 0.5–0.6 wt%. The concentrations of the main substances in the process water are listed in Table 2. The variation in concentration and composition during the sampling time was relatively modest, as can be seen from the table.

The SS in the process water consisted mainly of short fibers and wood fines that pass through the screens used in the dewatering stage of the TMP process. The particles in the process water had a broad size distribution, ranging from 0.9 to 735 μm; the main part being around 40 μm.

D-Mannose, D-glucose, and D-galactose, and low concentrations of L-arabinose and D-xylose were found after acid hydrolysis of the process water. The predominant hemicelluloses in softwood are GGM, arabinoglucuronoxylan (AGX) and arabinogalactan (AG) [23]. The monomeric sugar ratio mannose:glucose:galactose in GGM is typically around 3:1:0.5; the ratio xylose:glucuronic acid:arabinose in AGX around 10:2:1.3 and the ratio galactose:arabinose in AG around 6:1 [23]. By assuming these ratios for the hemicelluloses present in the process water the concentration of GGM, AGX and AG can be estimated from the monomeric sugar concentrations after acid hydrolysis to approximately 1.04 g/l, 0.05 g/l and 0.12 g/l, respectively. In addition to hemicelluloses, softwood contains minor amounts of other polysaccharides, the main ones being starch and pectic substances. Thus, starch and pectic substances may account for a minor part of the total polysaccharide concentration in the process water.

The molecular mass distribution of carbohydrates and lignin was determined by SEC. The number-averaged ($\bar{M}_n$) and weight-averaged ($\bar{M}_w$) molecular mass and polydispersity ($\bar{M}_w/\bar{M}_n$) of carbohydrates (measured as RI response) were 7 kg/mol, 26 kg/mol and 3.7, respectively. The corresponding values for lignin (measured as UV absorbance) were 1 kg/mol, 2 kg/mol and 1.9. The molecular mass distribution of carbohydrates and lignin is shown in Fig. 2.

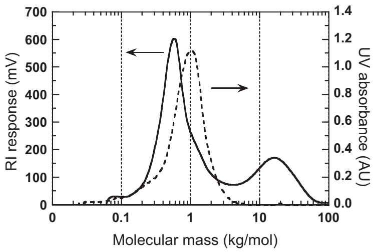

Fig. 2. Chromatographs from SEC analysis of TMP process water. Carbohydrates were detected by an RI detector (solid line) and lignin by the absorbance of UV light at 280 nm (dashed line). PEG standards were used for calibration.

The mean molecular mass of polysaccharides, GGM and lignin was determined by analyzing the concentration of sugars and lignin in nine SEC fractions. The molecular mass of a fraction is defined as the average of the highest and lowest molecular mass of PEG in the fraction. The cumulative distributions are shown in Fig. 3. The mean molecular masses of GGM and lignin were 9 kg/mol and 0.5 kg/mol, respectively.

The SEC fractions containing polysaccharides with molecular masses greater than 7.7 kg/mol were composed of D-mannose, D-glucose, and D-galactose, with a sugar unit ratio of about 3:1:0.5, which is representative of GGM [23,24]. Hence, the second RI peak in Fig. 2 represents high-molecular-mass GGM. The first RI peak in Fig. 2 indicates the presence of small saccharides in the process water. Saccharides with a molecular mass below 1 kg/mol contained very little, or no D-mannose subunits, but consisted mainly of subunits such as D-glucose, D-galactose, and L-arabinose; probably residues of pectic substances, starch and arabinogalactans. About 60–80% of the polysaccharides in the size range 1.0–7.7 kg/mol were GGM.

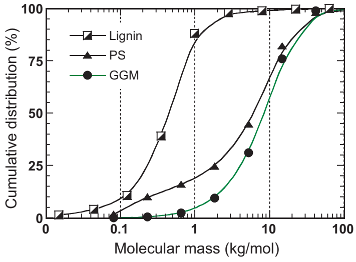

Fig. 3. Molecular mass distribution of lignin, polysaccharides (PS) and galactoglucomannan (GGM) in TMP process water determined by fractionation using SEC and analysis of the contents of lignin and sugar in each fraction.

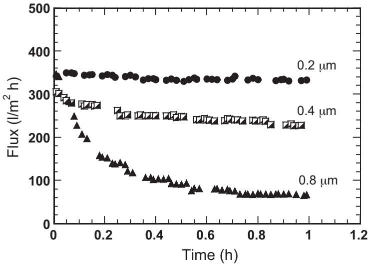

Fig. 4. Influence of membrane pore size on flux during microfiltration of TMP process water. The process water was filtered through a 1 mm mesh before microfiltration.

4.2. *Influence of membrane pore size*

The performance of the three MF membranes with pore sizes of 0.2, 0.4 and 0.8 μm was investigated in Unit II. The transmembrane pressure was 0.5 bar, the cross-flow velocity 4 m/s, and the temperature 80 °C.

The flux decline when treating the process water increased with increasing pore size, as shown in Fig. 4. The higher flux decline of the membranes with the larger pore size is probably due to more severe blocking of the pores in these membranes [25]. In addition to the lower flux, fouling of the 0.4 and 0.8 μm membranes was irreversible. The pure water flux of the membranes was not recovered even after several cleaning cycles. Membranes with 0.2 μm pores were therefore used in the following studies.

The retention of SS was 100%, and the retention of lignin was 14%, 15% and 11% for the 0.2, 0.4, and 0.8 μm membranes, respectively. The retention of hemicelluloses was considerably higher than expected. The hydrodynamic diameter of GGM with a molecular mass of 9 kg/mol is 9 nm, according to Eq. (5). The true retention (see Eq. (2)) of the 0.2 μm membrane would thus be <10%, whereas the observed retention of the 0.2, 0.4 and 0.8 μm membranes was 51%, 35% and 28%. The observed retention is always lower than the true retention because $C_m \geq C_b$.

The observed retention of PEG4 and PEG40, which were used for calibration of the molecular mass of hemicelluloses during SEC, was measured for the 0.2 μm membrane in Unit I. The transmembrane pressure was 0.5 bar and the cross-flow velocity 2 m/s. Retention for PEG4 and PEG40 was 0.5% and 6%, respectively and in agreement with the specifications of the membrane. This confirms that the high retention of hemicelluloses during MF of process water is not due to the size of hemicelluloses.

4.3. *Influence of particle size and pH*

Retention is known to increase when a cake layer is formed on the membrane surface. Particle size, as well as thickness and density of the cake layer, influence the retention. Furthermore, pH of the feed can influence retention since it has an effect on solute solubility and on interaction between solutes and the membrane. In order to study the influence of cake formation and pH, process water, pH adjusted process water and DF filtrate were microfiltered in Unit I. The transmembrane pressure was 0.3 bar, the cross-flow velocity 1.5 m/s, and the temperature 50 °C.

If the SS form a cake layer on the membrane, GGM can be retained by this layer. In order to reduce the amount of SS that could form a cake, DF was performed with a 10 μm filter cloth. About 90% of the SS were removed from the process water during DF, while the retention of GGM and lignin was insignificant. Not only the concentration of SS was decreased during DF (from 1.16 g/l to 0.13 g/l), but also the particles in the DF filtrate were considerably smaller than in the original process water, as can be seen in Fig. 5.

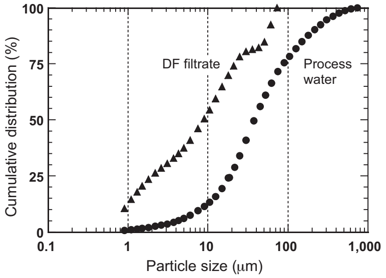

Fig. 5. Distribution of particle sizes in TMP process water and in drum filtration (DF) filtrate.

Surprisingly, the retention of GGM was higher during MF of DF filtrate, despite the fact that the concentration of SS was considerably lower. The retention of GGM was about 44% during MF of process water, and about 50% during MF of DF filtrate. The flux during MF was higher for the process water than the DF filtrate, as shown in Fig. 6. This is probably due to the formation of a denser cake layer on the membrane surface when treating DF filtrate containing smaller particles. A denser cake layer might also explain the somewhat higher retention of GGM during MF of DF filtrate.

The pH of the process water at the pulp mill is 4.2. The influence of pH was studied by adjusting the pH with NaOH to pH 6. The retention was about 44% for both the original and the pH adjusted process water. No significant difference in flux was observed, as shown in Fig. 6.

In spite of the negative influence on membrane performance during MF, DF will probably be needed as a form of pretreatment when concentrating process water. DF was therefore used in subsequent studies.

4.4. *Influence of cross-flow velocity*

Operating at high cross-flow velocity is a common way of reducing the influence of a cake layer on membrane performance. At high cross-flow velocity the thickness of the cake layer is decreased due to the increased shear rate on the membrane surface, in most cases resulting in higher fluxes and better separation.

A study of the influence of cross-flow velocity was performed in Unit II at 80 °C. The experiment was begun at 5 m/s (Re 84,700)

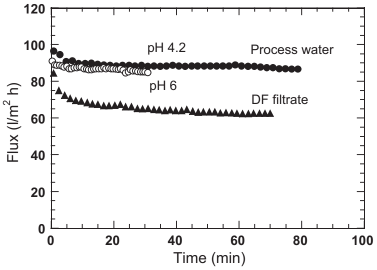

Fig. 6. Flux during microfiltration of process water (pH 4.2), pH adjusted process water (pH 6) and drum filtration (DF) filtrate with a 0.2 μm membrane.

and 0.3 bar. The transmembrane pressure was increased in steps of 0.2 bar up to 1.1 bar. The same procedure was repeated at 3 m/s (Re 50,800).

Increasing the cross-flow velocity did indeed have a positive effect on the flux, as shown in Fig. 7. At 5 m/s the flux still increased with increasing pressure in the pressure interval studied. In contrast, the shear rate at 3 m/s was not sufficient to prevent suspended particles forming a cake layer that caused the flux to level off at only 0.5 bar.

The observed retention of hemicelluloses was high, irrespective of the cross-flow velocity. A slight decrease in the retention with increasing pressure was noticed at 3 m/s, but the retention was still >60%.

4.5. *Influence of backpulsing*

In order to make use of the cake-reducing effect of backpulsing, it is important to optimize the system. The backpulsing parameters studied in this investigation were pulse length and forward filtration time (the time between two pulses), as both are known to have a considerable influence on backpulsing efficiency [26–28]. The transmembrane pressure was 1.1 bar and the temperature 80 °C during the experiment, which was carried out in Unit II. Without backpulsing, the flux was 300 l/m^2 h at 3 m/s and 480 l/m^2 h at 5 m/s. The retention was 59% at 3 m/s and 64% at 5 m/s.

The normalized flux and retention of hemicelluloses at various values of forward filtration time and backpulse duration can be seen in Fig. 8. Backpulsing had a positive effect on both flux and retention at 3 m/s, whereas the effect was insignificant, or even negative, at 5 m/s. The positive effect of backpulsing at 3 m/s is due to the presence of a cake that reduces the flux during MF without backpulsing at 3 m/s, as can be seen in Fig. 7. At 5 m/s the influence of the cake is of minor importance, and hence, the positive effect of backpulsing is less.

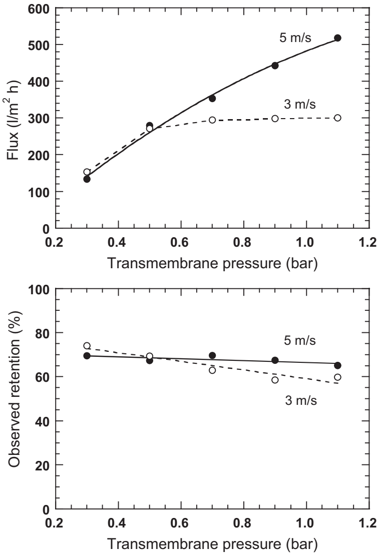

Fig. 7. Influence of cross-flow velocity and transmembrane pressure on flux and observed retention of hemicelluloses during microfiltration of TMP process water with a 0.2 μm membrane. The process water was drum filtered before the experiment.

Closing the permeate valve during backpulsing decreases the total time of forward permeate flow, which in turn decreases the average flux. Longer forward filtration time and pulse duration increase the negative effect on average flux. The negative effect of too long a pulse duration at 5 m/s can be seen in Fig. 8c. Almost 40% higher flux was obtained during backpulsing at 3 m/s compared to conventional MF. However, the retention of hemicelluloses was only reduced from 59% to 50%.

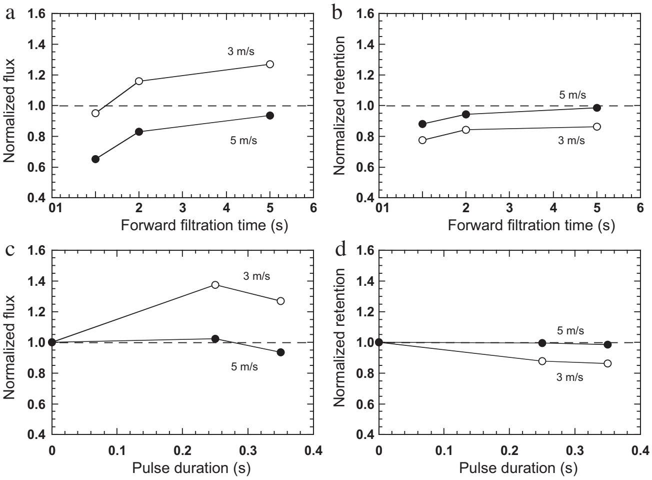

Fig. 8. Influence of forward filtration time and pulse duration on normalized flux and normalized hemicellulose retention during MF of TMP process water with a 0.2 μm membrane. The process water was drum filtered before the experiments.

The limited influence of cross-flow velocity and backpulsing on the retention of hemicelluloses indicates that it is not cake filtration that causes the high retention during MF of TMP process water. Another possible fouling mechanism that can reduce retention is continuous blocking of the membrane pores by foulants (e.g. extractives and lignin) deposited on the pore walls. Adsorption of extractives and lignin on solid surfaces will be studied by means of ellipsometry.

5. Conclusions

TMP waste water contains substances of various sizes: short fibers and fines >1 μm, colloidal wood resins 0.1–1 μm, GGM with a mean molecular mass of 9 kg/mol (d_h 9 nm), and lignin with a mean molecular mass of 0.5 kg/mol (2 nm). Dispersed substances were retained by a 0.2 μm membrane, while the retention of lignin was low, <15%. However, the retention of GGM was high (>50%), despite the fact that GGM molecules are much smaller than the membrane pores. The high retention of GGM is believed to be due to the blocking of membrane pores or the deposition of foulants on the pore walls, and not to cake filtration.

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References

[1] I. Gabrielii, P. Gatenholm, Preparation and properties of hydrogels based on hemicelluloses, J. Appl. Polym. Sci. 68 (1998) 1661–1667.
[2] I. Gabrielii, P. Gatenholm, W.G. Glasser, R.K. Jain, L. Kenne, Separation, characterization and hydrogel-formation of hemicellulose from aspen wood, Carbohydr. Polym. 43 (2000) 367–374.
[3] A. Höije, M. Gröndahl, K. Tømmeraas, P. Gatenholm, Isolation and characterization of physicochemical and material properties of arabinoxylans from barley husks, Carbohydr. Polym. 61 (2005) 266–275.
[4] M.S. Lindblad, A.-C. Albertsson, E. Ranucci, M. Laus, E. Giani, Biodegradable polymers from renewable sources: rheological characterization of hemicellulose-based hydrogels, Biomacromolecules 6 (2005) 684–690.
[5] J. Hartman, A.-C. Albertsson, M.S. Lindblad, J. Sjöberg, Oxygen barrier materials from renewable sources: material properties of softwood hemicellulose-based films, J. Appl. Polym. Sci. 100 (2006) 2985–2991.
[6] N.M.L. Hansen, D. Plackett, Sustainable films and coatings from hemicelluloses: a review, Biomacromolecules 9 (2008) 1493–1505.
[7] K. Sundberg, B. Holmbom, C. Eckerman, M. Adams, Method for recovering non-fibrous substances from wood material. Patent application PCT/WO0240767 (2002).
[8] S. Willför, P. Rehn, A. Sundberg, K. Sundberg, B. Holmbom, Recovery of water-soluble acetylgalactoglucomannans from mechanical pulp of spruce, Tappi J. 2 (2003) 27–32.
[9] T. Persson, H. Krawczyk, A.-K. Nordin, A.-S. Jönsson, Fractionation of process water in thermomechanical pulp mills, Bioresour. Technol. 101 (2010) 3884–3892.
[10] R. Ekman, B. Holmbom, Analysis by gas chromatography of the wood extractives in pulp and water samples from mechanical pulping of spruce, Nord. Pulp Pap. Res. J. 4 (1) (1989) 16–24.
[11] F. Örså, B. Holmbom, J. Thornton, Dissolution and dispersion of spruce wood components in hot water, Wood Sci. Technol. 31 (1997) 279–290.
[12] A. Sundberg, A. Pranovich, B. Holmbom, Chemical characterization of various types of mechanical pulp fines, J. Pulp Pap. Sci. 29 (2003) 173–178.
[13] S. Willför, R. Sjöholm, C. Laine, M. Roslund, J. Hemming, B. Holmbom, Characterisation of water-soluble galactoglucomannans from Norway spruce wood and thermomechanical pulp, Carbohydr. Polym. 52 (2003) 175–187.
[14] S. Willför, A. Sundberg, J. Hemming, B. Holmbom, Polysaccharides in some industrially important softwood species, Wood Sci. Technol. 39 (2005) 245–258.
[15] A. Pranovich, M. Reunanen, R. Sjöholm, B. Holmbom, Dissolved lignin and other aromatic substances in thermomechanical pulp waters, J. Wood Chem. Technol. 25 (2005) 109–132.
[16] C. Xu, S. Willför, K. Sundberg, C. Petterson, B. Holmbom, Physico-chemical characterization of spruce galactoglucomannan solutions: stability, surface activity and rheology, Cell. Chem. Technol. 41 (2007) 51–62.
[17] C. Xu, A. Pranovich, J. Hemming, B. Holmbom, S. Albrecht, H.A. Schols, S. Willför, Hydrolytic stability of water-soluble spruce O-acetyl galactoglucomannans, Holzforschung 63 (2009) 61–68.
[18] M. Meireles, A. Bessieres, I. Rogissart, P. Aimar, V. Sanchez, An appropriate molecular size parameter for porous membranes calibration, J. Membr. Sci. 103 (1995) 105–115.
[19] T. Ehrman, Laboratory analytical procedure LAP-001: standard method for determination of total solids in biomass, NREL, Midwest Research Institute for the Department of Energy, USA, 1994.
[20] T. Ehrman, Laboratory analytical procedure LAP-005: standard method for ash in biomass, NREL, Midwest Research Institute for the Department of Energy, USA, 1994.
[21] R. Ruiz, T. Ehrman, Laboratory analytical procedure LAP-014: dilute acid hydrolysis procedure for determination of total sugars in the liquid fraction of process samples, NREL, Midwest Research Institute for the Department of Energy, USA, 1996.
[22] M. Björklund Jansson, et al., 2008, Two methods for extraction and GC-analysis of lipophilic wood extractives. Report No 3 of the Nordic Standardization Program (NSP).
[23] E. Sjöström, Wood Chemistry – Fundamentals and Applications, second ed., Academic press, San Diego, 1993.
[24] S. Willför, K. Sundberg, M. Tenkanen, B. Holmbom, Spruce-derived mannans – a potential raw material for hydrocolloids and novel advanced natural materials, Carbohydr. Polym. 72 (2008) 197–210.
[25] K.J. Hwang, C.Y. Liao, K.L. Tung, Effect of membrane pore size on the particle fouling in membrane filtration, Desalination 234 (2008) 16–23.
[26] V.G.J. Rodgers, R.E. Sparks, Reduction of membrane fouling in the ultrafiltration of binary protein mixtures, AIChE J. 37 (1991) 1517–1528.
[27] S.G. Redkar, R.H. Davis, Cross-flow microfiltration with high-frequency reverse filtration, AIChE J. 41 (1995) 501–508.
[28] C.S. Parnham, R.H. Davis, Protein recovery from bacterial cell debris using cross-flow microfiltration with backpulsing, J. Membr. Sci. 118 (1996) 259–268.

Paper III

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Combined membrane filtration and enzymatic treatment for recovery of high molecular mass hemicelluloses from chemithermomechanical pulp process water

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HIGHLIGHTS

- Hemicelluloses were recovered from chemithermomechanical pulp process water.
- Membrane filtration and enzymatic treatment were used in an innovative process.
- Membrane filtration provided a hemicellulose fraction suitable for enzymatic treatment.
- Enzymatic laccase treatment increased the molecular mass of hemicelluloses markedly.
- Large hemicelluloses were separated from small hemicelluloses by ultrafiltration.

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ABSTRACT

Hemicelluloses with high molecular mass are needed for the manufacture of value added products such as food packaging barrier films. In this work such molecules were recovered from chemithermomechanical pulp (CTMP) process water using an innovative three-stage process comprising membrane separation and enzymatic treatment with laccase. Microfiltration followed by ultrafiltration was found to be a suitable combination in the first stage, providing a concentrated and purified hemicellulose fraction suitable for enzymatic treatment. In both membrane processes a high average flux (260 and 115 l/m^2 h) and a low fouling tendency were observed. A marked increase in the average molecular mass of hemicelluloses with bound lignin moieties was achieved by laccase treatment in the second stage. The enzymatically cross-linked hemicelluloses were finally recovered in the third stage using ultrafiltration. In the final high molecular mass solution the hemicellulose concentration was 54 g/l, the contribution of hemicelluloses to the total solids content 43%, and the viscosity of the solution 27 mPa s. The results demonstrate that a hemicellulose fraction of high quality can be produced from CTMP process water, and that this could constitute a suitable feedstock for the production of, for example, barrier films for renewable packaging.

1. Introduction

During the production of thermomechanical pulp and chemithermomechanical pulp (CTMP), hemicelluloses and other wood components are partly extracted and dissolved in the process water [1–3]. Although, their concentration in the process water is low (often only ~ 1 g/l), the total amount is considerable as the flow rate of process water in a pulp mill is commonly several hundred cubic meters per hour. Recent research has revealed that hemicelluloses originating from wood are valuable molecules that could be used in various value added applications, such as barrier films and coatings [4–7], hydrogels [8] and paper additives [9,10]. As a consequence of the growing range of applications of hemicelluloses, as well as their availability at high quantities in pulp mills, the recovery of these molecules from process water in thermomechanical pulp and CTMP mills is becoming increasingly attractive within the pulp and paper industry.

The process water in pulp mills is commonly a complex mixture of wood constituents such as hemicelluloses, lignin, wood extractives and organic acids (e.g. pectic acid and acetic acid) [1,11]. In order to obtain a purified fraction of hemicelluloses, these molecules must be separated from the other constituents in the mixture. Membrane filtration is one of the most selective and energy-efficient separation techniques available, and could therefore be suitable for this kind of separation. Ultrafiltration has been used successfully to recover hemicelluloses from hot water hydro-

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lysate of softwood [4,7,12,13] and mechanical pulp [14,15]. Our group has worked extensively with thermomechanical pulp process water, and developed a multi-stage procedure comprising microfiltration and ultrafiltration for the recovery of hemicelluloses [16–18]. Although ultrafiltration of process water from CTMP mills has been studied [11,19,20], to the best of our knowledge, no investigations have yet been performed on the recovery of hemicelluloses from this type of process water.

One of the major goals of previous work has been to obtain a fraction of high molecular mass hemicelluloses, as large molecules are considered to be suitable for the manufacture of many value added products such as barrier films and coatings [18,21]. However, the process water in pulp mills usually contains hemicelluloses with a rather low molecular mass and broad size distribution [21]. An efficient approach to producing a high quality hemicellulose fraction from pulp mill process water could, therefore, be to increase their molecular size during recovery. Enzymatic treatment with laccase has previously been shown to increase the molecular mass of phenolic contaminants [22] and lignosulfonates [23] originating from pulp and paper effluents. This increase was mainly explained by the oxidation of phenolic end groups, resulting in the formation of radicals and their subsequent coupling to larger polymers. In a recent patent by Henriksson et al. [24], it was reported that laccase could also be used to increase the molecular mass of hemicelluloses to which aromatic moieties were attached.

In the present work, an innovative process for the production of a hemicellulose fraction comprising large molecules was developed for CTMP process water. The key elements of this process are microfiltration, ultrafiltration and enzymatic treatment with laccase. The performance of each membrane filtration stage of the process was investigated on a small pilot scale. The influence of laccase treatment on the molecular mass of hemicelluloses and the rheological properties of the solution was also studied.

2. Materials and methods

2.1. Process description

A schematic of the process used in this investigation is shown in Fig. 1. First, hemicelluloses in CTMP process water were separated from other wood constituents using microfiltration and ultrafiltration. The concentrated and purified hemicellulose fraction was subsequently treated with the laccase enzyme, capable of crosslinking hemicellulose molecules to which lignin moieties are already bound. A second ultrafiltration step was carried out to separate crosslinked hemicelluloses with high molecular mass from those with low molecular mass.

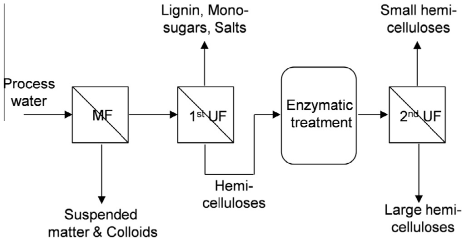

Fig. 1. Schematic of the process used in this work. (MF and UF denote microfiltration and ultrafiltration.).

2.2. Process water

The process water was withdrawn from the pulping process of a CTMP mill located in Sweden. The raw material used in the mill is spruce wood, and the pulp produced is used to manufacture packaging board. The total flow of process water in the pulp mill is approximately 400 m^3/h.

2.3. Equipment

2.3.1. Membranes for microfiltration and ultrafiltration

The specifications of the membranes used for microfiltration and ultrafiltration are summarized in Table 1. The microfiltration membrane was a tubular ceramic membrane manufactured by Atech Innovations GmbH (Gladbeck, Germany). This membrane had seven parallel feed channels, each with an inner diameter of 6 mm. The total length of the membrane tube was 1 m and the outer diameter 25 mm. Spiral wound elements (Alfa Laval Nordic A/S, Søborg, Denmark) equipped with a 48-mil spacer were used in both ultrafiltration stages. The UF membranes were made of the same material, but differed in their nominal molecular weight cut-off (MWCO). Both spiral elements had an outer diameter of 64 mm and a length of 0.43 m.

2.3.2. Membrane filtration setups

Different experimental setups were used for microfiltration and ultrafiltration. Both setups consisted of two tanks, a circulation pump and a membrane module, in which the microfiltration or ultrafiltration membrane was inserted. The first tank was used as the feed tank during the experiments, and the second tank was only used during cleaning cycles. The setups were equipped with pressure transmitters (dTrans p02, Jumo AB, Helsingborg, Sweden) installed on the feed and the retentate side of the membrane modules. In the microfiltration setup an additional pressure transmitter was installed on the permeate side. Temperature probes were immersed in the feed tanks, and electronic balances (PL6001-S, Mettler Toledo Inc., Columbus, OH) were used to measure the permeate flows through the membranes gravimetrically. In the microfiltration setup a volume flow meter (Fischer&Porter Co. Ltd., Göttingen, Germany) was installed on the feed line, while a rotameter was used to measure the retentate flow in the ultrafiltration setup. The systems were pressurized by a valve installed on the retentate side of the modules, and the transmembrane pressure (TMP) was calculated as the difference between the average pressure on the feed and retentate side, and the pressure on the permeate side of the membrane. The cross-flow in the feed flow channels of the membranes could be adjusted in both setups by the pump speed using frequency converters. All data from the measuring devices were recorded continuously using LabView software (National Instruments Co., Austin, TX).

2.4. Experimental procedure

2.4.1. Membrane preparation

Clean membranes were used in all experimental studies in this work. The ceramic microfiltration membrane was cleaned for 60 min with a 0.7 wt.% solution of the alkaline cleaning agent Ultrasil 11 (Ecolab AB, Älvsjö, Sweden). The ultrafiltration membranes were instead cleaned for 45 min with a 0.4 wt.% solution of the alkaline cleaning agent Ultrasil 10 (Ecolab AB). The temperature during cleaning was 50 °C, and membranes were rinsed thoroughly with deionized water after cleaning until no cleaning agent was left in the system. The performance of the membranes was controlled before each study by measuring the pure water flux using deionized water at 30 °C.

Table 1
Specifications of the membranes used for microfiltration and ultrafiltration.

	Microfiltration	1st Ultrafiltration	2nd Ultrafiltration
Membrane	7/6	UFX5pHt	UFX10pHt
Membrane material	α-Alumina oxide	Hydrophilized polysulfone	Hydrophilized polysulfone
Filtration area	0.13 m^2	0.7 m^2	0.7 m^2
Pore size/MWCO	0.2 μm	5 kDa	10 kDa
Range of pH resistance	1–14	1–13	1–13
Maximum temp.	>100 °C	75 °C	75 °C
Maximum pressure	10 bar	15 bar	15 bar

2.4.2. Microfiltration and first ultrafiltration stage

In order to remove fiber residues that could block the feed flow channels of the microfiltration membrane, pulp mill process water was first prefiltered through a 250 μm screen. About 950 l of the prefiltered water was collected and subsequently used in the microfiltration stage. Microfiltration was started by circulating 190 l of the total volume in the microfiltration setup at a temperature of 60 °C with the permeate valve closed. The cross-flow velocity was adjusted to 5 m/s, and the permeate valve was opened carefully to adjust the TMP to 0.7 bar. Initially, the retentate and the permeate stream were recirculated to the feed tank for 30 min in order to stabilize the system. The permeate stream was then withdrawn under constant operating conditions throughout the remaining time of the study. The level in the feed tank was kept constant by continuously pumping the remaining process water into the feed tank. When the entire volume had been added, the liquid level in the feed tank was allowed to decrease until the total volume in the system was too small to allow further volume reduction. Microfiltration was interrupted twice during the night due to the long duration of the experiment (the total filtration time was 32 h). During each of these interruptions the permeate valve was closed, the temperature reduced to 50 °C, and the feed was circulated in the system for about 12 h. Microfiltration was then continued under the same operating conditions as before the interruption, without cleaning of the membrane. In total, about 930 l of permeate was collected during the microfiltration experiment.

Hemicelluloses in the microfiltration permeate were concentrated by ultrafiltration using the UFX5pHt membrane (cut-off 5 kDa). The initial feed volume of 930 l was reduced to a final volume of 30 l by continuously withdrawing ultrafiltration permeate. The general procedure during ultrafiltration was the same as during microfiltration. The cross-flow rate and the temperature were 1.3 m^3/h and 60 °C, respectively. The TMP, adjusted with the valve on the retentate side of the module, was 5 bar. The total duration of ultrafiltration was about 16 h, and was carried out without interruption.

2.4.3. Enzymatic treatment and second ultrafiltration stage

About 29 l of the retentate from the first ultrafiltration stage was treated with a laccase enzyme in order to increase the molecular mass of the hemicelluloses in the solution. Enzymatic treatment was carried out in a glass reactor equipped with an agitator (ReactoMate 30000 CLR, Asynt Ltd., Cambridgeshire, UK). Before the addition of laccase, the pH and the temperature of the solution were adjusted to provide appropriate reaction conditions. The initial pH of 6.0 was lowered to 4.5 by the addition of dilute sulfuric acid. The temperature of the solution was increased and maintained at 40 °C by circulating temperature-adjusted water around the glass reactor. The reaction was subsequently started by adding 20 U/g substrate (1.4 mg/g) of the laccase enzyme (Sigma 51639, Sigma–Aldrich Chemie GmbH, Steinheim, Germany) to the solution. During the total reaction time of 3 h, pure oxygen gas was continuously bubbled through the solution.

After enzymatic treatment of the ultrafiltration retentate, large hemicellulose molecules were separated from smaller hemicelluloses in a second ultrafiltration stage using the UFX10pHt membrane (cut-off 10 kDa). The initial feed volume was 28 l, and the solution was concentrated at a constant cross-flow rate of 1.2 m^3/h, a temperature of 60 °C, and a TMP of 3 bar. The final volume in the feed tank was 7 l, and the duration of the final ultrafiltration stage about 3 h.

2.5. Analytical methods

2.5.1. Total solids, ash and suspended matter

Samples were dried for 24 h in an oven at 105 °C. The total solids content was then determined from the dry weight of the residue. The dry sample was further heated to 575 °C, and this temperature was maintained for 3 h. After cooling to room temperature, the ash content was determined gravimetrically. The concentration of suspended matter was determined by filtration of a sample through a 1 μm filter (GF/B, Whatman Int. Ltd., Maidstone, UK). Suspended matter was then defined as the dry mass of the particles retained by the filter.

2.5.2. Hemicelluloses and lignin

Samples were filtered through a 1 μm filter (GF/B, Whatman Int. Ltd.) in order to remove particles before analyzing the concentration of hemicelluloses and lignin. The concentration of hemicelluloses was determined by first degrading hemicellulose molecules to monomeric sugars using a standardized method for acid hydrolysis [25]. The concentration of the monomeric sugars D-galactose, D-glucose, D-xylose, D-mannose and L-arabinose was then measured using high-performance anion-exchange chromatography coupled with pulsed amperometric detection. The chromatography system (ICS-3000, Dionex Corp., Sunnyvale, CA) was equipped with a Carbo Pac PA1 analytical column. Deionized water was used as eluent at a flow rate of 1 ml/min, and the column was cleaned with a solution of 200 mM sodium hydroxide (NaOH) dissolved in 170 mM sodium acetate. The sample injection volume was 10 μl. The concentration of hemicelluloses was defined as the sum of the monomeric sugars after anhydro corrections of 0.88 and 0.90 for pentoses and hexoses, respectively.

The concentration of lignin was determined by measuring the UV absorbance at a wavelength of 280 nm in a spectrophotometer (UV-160, Shimadzu Corp., Kyoto, Japan). An extinction coefficient of 30 l/g cm, was used [26]. It should be noted that besides lignin, pectin degradation products have strong UV absorbance at 280 nm [1]. Thus, the presence of these substances could lead to an overestimation of the lignin concentration.

The molecular mass distribution of hemicelluloses and lignin was determined by size exclusion chromatography using a Waters 600E chromatography system (Waters, Milford, MA) equipped with a refractive index (RI) detector (model 2414, Waters) and a UV detector (model 486, Waters). The analytical column was packed with 30 cm Superdex 30 and 30 cm Superdex 200 (GE Healthcare, Uppsala, Sweden). A 125 mM NaOH solution was used as eluent at a flow rate of 1 ml/min. The system was calibrated with polyethylene glycol standards with peak molecular masses of 0.4, 4, 10 and 35 kg/mol (Merck Schuchardt OHG, Hohenbrunn, Germany).

2.5.3. Viscosity and turbidity

Viscosity measurements were performed in a rotational rheometer (StressTech, Reologica Instruments AB, Lund, Sweden) using a cup-and-bob geometry. The torque range of the rheometer was 0.05 μN m to 200 mN m. The system allowed the temperature of the sample to be kept constant during the measurements. The apparent viscosity was measured at a temperature of 60 °C in the shear rate range 1–100 s^{-1}.

The turbidity of a sample was measured in a turbidimeter (2100P ISO, HACH Co., Loveland, CO). The instrument was calibrated with stabilized formazin standards (HACH Co.) of 0, 20, 100 and 800 nephelometric turbidity units (NTUs).

3. Results and discussion

3.1. Composition of the process water

The major components of the CTMP process water used in this study were suspended matter, ash, lignin and hemicelluloses, as can be seen in Table 2. The concentration of hemicelluloses was about 0.8 g/l, i.e. roughly 10% of the total solids. Hemicelluloses consisted mainly of the monosaccharides mannose, glucose and galactose, indicating that the major hemicellulose in the process water was galactoglucomannan. The presence of this hemicellulose was expected as it is the most abundant one in spruce wood [27], the raw material used by the pulp mill from which the process water was obtained. It has been shown in earlier studies that wood extractives, pectins, acetic acid and methanol are also released into the process water in CTMP mills [1,2]. Especially the wood extractives can be present at rather high concentration. For example, Puro et al. reported a concentration of lipophilic wood extractives of 1.65 g/l in CTMP process water [11]. These substances are known to be dissolved as well as dispersed as droplets, forming colloids with a size around 0.1–2 μm [11]. In the process water used in the present study it can therefore be assumed that wood extractives also constitute part of the total solids.

3.2. Removal of suspended matter and colloids

From the results of the composition analysis given in Table 2, it can be seen that various substances must be removed from the process water in order to recover hemicelluloses as a product. Constituents with a larger size than hemicelluloses are mainly suspended matter and colloids. These impurities were first separated from the process water by prefiltration and microfiltration. After prefiltration through a 250 μm screen, the concentration of suspended matter was reduced from 3.3 g/l to less than 1.0 g/l. Residual suspended matter and colloids were effectively removed during microfiltration. No suspended matter was found in the microfiltration permeate. Furthermore, the turbidity was reduced from 2000 NTU to less than 3 NTU. Previous research has shown that the turbidity of pulp mill process water after the removal of suspended matter is correlated with the concentration of wood resins in the water [28]. Thus, the low turbidity in the microfiltration permeate indicates that some of the wood extractives were retained by the microfiltration membrane. High retention of the wood extractives, i.e. fatty acids, resin acids, sterols and steryl esters, has been observed previously, for example, by Persson et al. during microfiltration of thermomechanical pulp process water [18].

Apart from suspended matter and colloids, some of the hemicelluloses were also retained by the membrane, leading to a loss of hemicelluloses during microfiltration. The initial retention of hemicelluloses was about 30%, and retention was found to increase to almost 80% with increasing volume reduction. Despite this marked retention, more than 75% of the hemicelluloses could be recovered in the permeate. This acceptably high yield was mainly achieved because of the high volume reduction achieved during microfiltration (∼98%). The average flux during microfiltration was ∼260 l/m^2 h, and thus rather high. As can be seen in Fig. 2 the flux decline was only minor for a volume reduction below 90%, but flux declined steeply when the volume reduction exceeded 90%. This flux decline was expected, and can be explained mainly by the high increase in the concentration of suspended matter in the retentate (see Fig. 2).

Table 2
Composition of the CTMP process water used in this study.

	Concentration (g/l)	Percentage of total solids (%)
Total solids	8.01	–
Suspended matter	3.25	40.6
Ash	1.85	28.7
Lignin	1.30	16.2
Hemicelluloses	0.79	9.9
Mannose[a]	0.46	
Glucose[a]	0.22	
Galactose[a]	0.13	
Arabinose[a]	0.04	
Xylose[a]	0.03	

[a] Concentration after acid hydrolysis.

3.3. Concentration of hemicelluloses

After the removal of suspended matter and colloids, the hemicelluloses can be assumed to have the highest molecular mass of the components remaining in the process water. Thus, hemicellulose molecules can be concentrated by ultrafiltration and separated from constituents with low molecular mass by choosing a membrane with a nominal MWCO smaller than the size of the hemicellulose molecules. A preliminary test (unpublished results) revealed that a membrane with a nominal MWCO of 5 kDa (UFX5pHt) resulted in markedly higher hemicellulose retention than a 10 kDa membrane (RC70PP and ETNA10PP, both from Alfa Laval). Thus, in order to obtain a high hemicellulose yield the 5 kDa membrane was used for concentration in this study.

Fig. 3 shows the retention of hemicelluloses and the impurity, lignin, during concentration using the UFX5pHt membrane. The

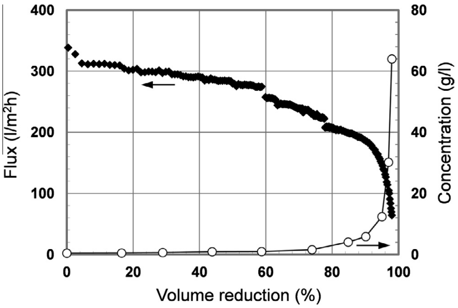

Fig. 2. Flux (diamonds) and concentration (circles) of suspended matter in the retentate during microfiltration of CTMP process water. The temperature, the transmembrane pressure and the cross-flow velocity were 60 °C, 0.7 bar and 5 m/s, respectively.

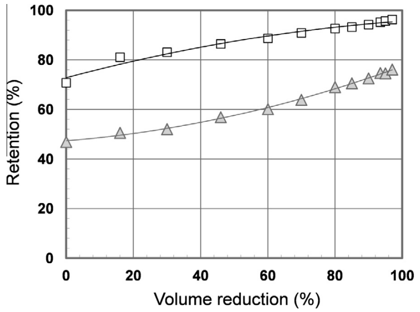

Fig. 3. Retention of hemicelluloses (squares) and lignin (triangles) during ultrafiltration using the UFX5pHt membrane (cut-off 5 kDa). Ultrafiltration was carried out at 60 °C, 5.0 bar and 1.3 m^3/h.

hemicellulose retention was in the range 70–96%. In contrast, the retention of lignin was markedly lower. Thus, while the concentration of hemicelluloses increased considerably from 0.6 to 14.0 g/l, the increase in lignin concentration was lower (from 0.8 to 7.4 g/l). It has previously been shown that lignin forms covalent linkages with hemicelluloses in spruce wood, resulting in lignin-carbohydrate complexes [29]. The lignin retention observed in this study can therefore be explained, to some extent, by the attachment of lignin moieties to hemicellulose molecules. Despite the formation of these complexes, the final ultrafiltration retentate contained about 74% of the hemicelluloses, but only 28% of the lignin molecules, showing that hemicelluloses were successfully purified at an acceptable yield during ultrafiltration.

It can also be seen in Fig. 3 that the retention of hemicelluloses and lignin molecules increased markedly with increasing volume reduction. A possible explanation of this observation could be that the average molecular mass of both hemicelluloses and lignin molecules increased. Fig. 4 shows the size distribution of these molecules in the retentate at volume reductions of 0%, 70% and 97%. It can be seen that a considerable proportion of molecules with low molecular mass (~1 kDa) was present at the beginning of concentration (volume reduction 0%), while only a few molecules of this size were found in the retentate at a volume reduction of 97%. This indicates that mainly small molecules, less suitable for value added applications, were lost in the ultrafiltration permeate. In the final retentate, hemicelluloses ranging from 2 to 20 kDa, and lignin molecules ranging from 1 to 4 kDa were predominant.

The initial flux during ultrafiltration was almost 170 l/m^2 h, and the fouling tendency was low, as can be seen in Fig. 5. As a consequence, the high volume reduction of 97% could be achieved without intermediate cleaning of the membrane. It has been reported in a study by Puro et al. that polymeric membranes were irreversibly fouled during ultrafiltration of CTMP process water [19]. However, this was not observed in the present study, as the same pure water flux was measured before and after the experiment. One reason for these contradictory results could be the high MWCO of the membranes used in the study by Puro et al. (30 and 50 kDa). Various researchers have found that the susceptibility of membranes to fouling increases with increasing pore size of the membrane during ultrafiltration [12,19].

3.4. Increasing the molecular mass by enzymatic treatment

As discussed previously, a high molecular mass is advantageous in the manufacture of value added products from hemicelluloses. In a previous study on the laboratory scale, it was demonstrated that the average molecular mass of spruce galactoglucomannans could be increased by utilizing enzyme-catalyzed crosslinking of aromatic moieties bound to hemicelluloses [24]. In the present work, we investigated whether it was possible to apply a similar principle on a larger scale using the hemicelluloses recovered from CTMP process water. Fig. 6 shows the molecular mass distribution of hemicelluloses and lignin molecules in the ultrafiltration retentate before and after enzymatic treatment. It can be seen that the peak molecular mass of hemicelluloses was initially about 4 kDa,

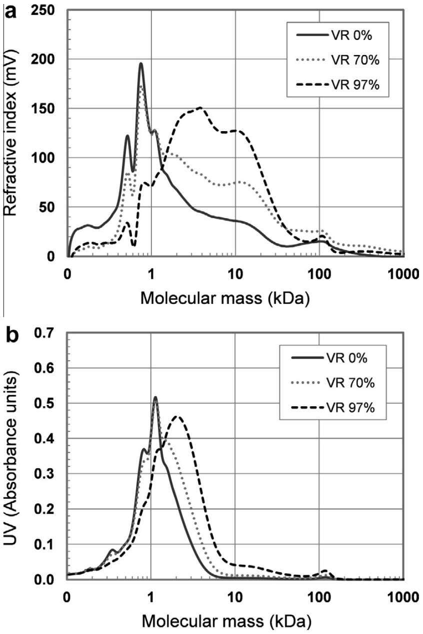

Fig. 4. Size distribution of (a) hemicelluloses (measured by RI) and (b) lignin (measured by UV) in the ultrafiltration retentate at a volume reduction (VR) of 0%, 70% and 97%.

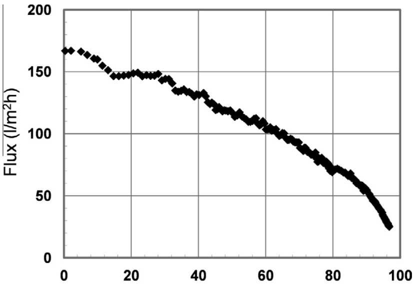

Fig. 5. Flux during the concentration of hemicelluloses with the UFX5pHt membrane (cut-off 5 kDa).

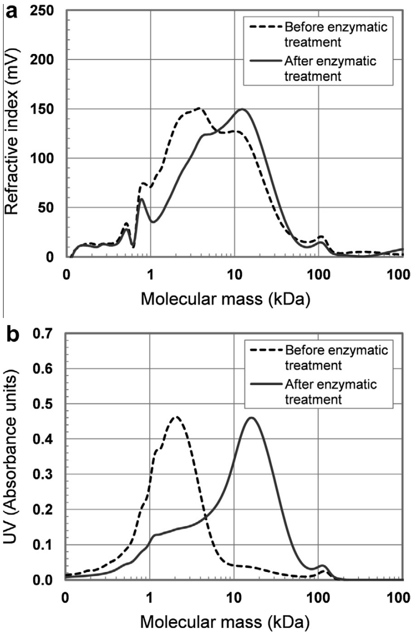

Fig. 6. Size distribution of (a) hemicelluloses (measured by RI) and (b) lignin (measured by UV) before and after enzymatic treatment of the final ultrafiltration retentate with laccase.

and increased to about 12 kDa following enzymatic treatment. Furthermore, laccase treatment had a considerable effect on the peak molecular mass of lignin molecules. These results suggest that hemicelluloses with bound lignin moieties were successfully crosslinked.

Furthermore, enzymatic treatment was found to slightly increase the viscosity of the solution, from 1.3 to about 1.7 mPa s (measured at a shear rate of 100 s^{-1} and a temperature of 60 °C). It can be assumed that the increase in molecular size and the change in the molecular structure as a result of crosslinking are responsible for this effect.

3.5. Purification of high molecular mass hemicelluloses

The laccase enzyme used for the enzymatic treatment is only capable of crosslinking hemicelluloses to which lignin moieties are attached [24]. As a consequence, some molecules with relatively low molecular mass were present after enzymatic treatment. Ultrafiltration was used to separate the larger crosslinked hemicelluloses from the smaller ones, as it is desirable to concentrate and purify crosslinked hemicelluloses as much as possible in the ultrafiltration retentate.

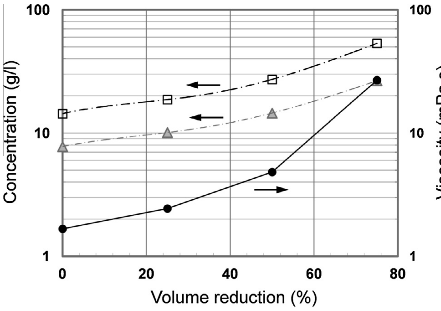

Fig. 7. Concentration of hemicelluloses (squares) and lignin (triangles) and viscosity of the retentate (dots) during purification of large hemicellulose molecules with the UFX10pHt membrane (cut-off 10 kDa).

About 90% of the total amount of hemicelluloses and lignin molecules in the solution after crosslinking were retained by the 10 kDa membrane used for ultrafiltration (UFX10pHt), indicating that molecules with a molecular mass below 10 kDa accounted for only a minor fraction of the hemicelluloses present. The high retention gave rise to a considerable increase in concentration in the retentate from ultrafiltration. As can be seen in Fig. 7, the concentrations of hemicelluloses and lignin molecules were initially about 14 and 7.5 g/l, respectively, and increased to about 53.5 and 27 g/l in the final retentate, at a volume reduction of 75%. Concomitant with concentration, a remarkable increase in the viscosity was observed (Fig. 7). The viscosity of the final retentate, measured at 100 s^{-1} and 60 °C, was 27 mPa s, and thus about 55 times higher than the viscosity of water. Xu et al. reported a lower viscosity of about 10 mPa s for a solution containing 50 g/l galactoglucomannan from thermomechanical pulp process water, although their measurements were carried out at a lower temperature of 25 °C [30]. The exceptionally high viscosity of the solution in the present work could be explained by the increased molecular mass of hemicelluloses due to enzymatic treatment.

The initial flux during ultrafiltration was about 32 l/m^2 h, and was thus of the same magnitude as the final flux before enzymatic treatment (see Fig. 5). As can be seen in Fig. 8, the flux declined markedly with increasing concentration of hemicelluloses in the retentate. When the hemicellulose concentration exceeded about 50 g/l, the flux fell below 10 l/m^2 h, indicating that it is difficult to achieve a higher hemicellulose concentration with the membrane used here. According to the film model, the theoretical concentration that could be achieved is about 85 g/l (obtained from the intercept of the straight line on the *x*-axis shown in Fig. 8).

The two fractions obtained after ultrafiltration differed markedly in composition, product purity and the size of the molecules, which suggests that they can be used in different applications. The concentration of hemicelluloses and lignin was high in the ultrafiltration retentate (53.5 g/l and 27 g/l), and their contributions to the total solids about 43% and 21%, respectively. Furthermore, it can be seen in Fig. 9 that the hemicelluloses and lignin molecules in this fraction were large and had almost the same molecular mass distribution, indicating that lignin molecules were largely attached to hemicelluloses. The concentration of hemicelluloses and lignin in the ultrafiltration permeate was significantly lower (3 g/l and 1.5 g/l), as was the proportion of the total solids (22% and 11%). The peak molecular mass of hemicelluloses and lignin molecules in the permeate fraction was only about 2 kDa, as can be seen in Fig. 9. Based on these findings, we believe that the retentate fraction could constitute an excellent feedstock for the manufacture of barrier films for food packaging, and that the permeate fraction could be suitable for less valuable products, such as the production of biogas and bioethanol. Preliminary tests revealed that non-brittle barrier films with low oxygen permeability could be fabricated from the retentate fraction without the need for the addition of high amounts of plasticizers. However, further work is still re-

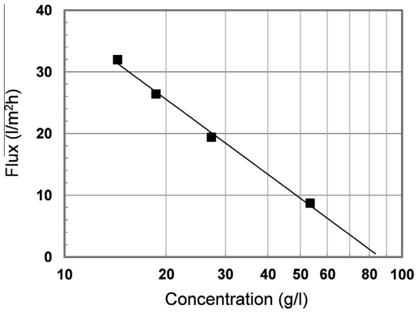

Fig. 8. Flux as a function of the hemicellulose concentration (note the logarithmic scale) in the retentate during ultrafiltration with the UFX10pHt membrane (cut-off 10 kDa). Ultrafiltration was carried out at 60 °C, 3.0 bar and 1.2 m^3/h.

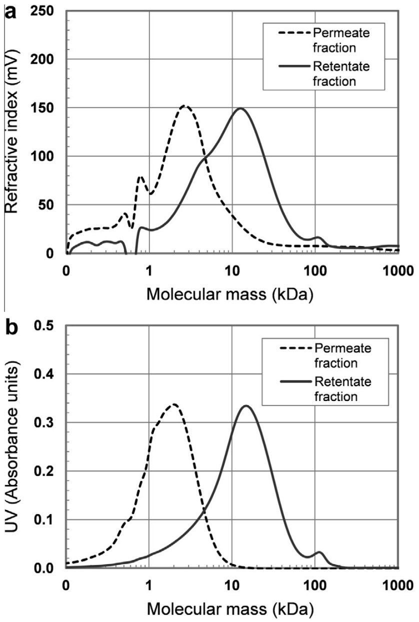

Fig. 9. Size distribution of (a) hemicelluloses and (b) lignin in the permeate and retentate following separation by ultrafiltration.

quired to demonstrate the suitability of this fraction and to investigate the properties of such films. Results of this ongoing work will be presented in an upcoming paper.

4. Conclusions

Hemicelluloses with high molecular mass were recovered from CTMP process water using a combination of membrane filtration and enzymatic treatment. The suspended matter and colloids in the process water were efficiently removed by microfiltration. Ultrafiltration proved to be a suitable method for concentrating and purifying hemicellulose molecules in the microfiltration permeate. A very high flux and a low fouling tendency were observed in both membrane processes, indicating that this procedure could be cost-efficient for hemicellulose recovery at a pulp mill.

The enzymatic treatment with laccase was found to successfully crosslink hemicellulose molecules with bound lignin moieties. As a consequence, the average molecular mass of hemicelluloses and lignin molecules, as well as the viscosity of the solution, increased markedly. It was shown that hemicelluloses with high molecular mass can be separated from those with low molecular mass after enzymatic treatment using an ultrafiltration membrane with a MWCO of 10 kDa. About 90% of all hemicelluloses were retained in the high molecular mass fraction, leading to high concentration (~54 g/l) and exceptionally high viscosity of the solution (~27 mPa s). The hemicelluloses in this fraction could provide an excellent feedstock for the manufacture of renewable barrier films that could replace fossil-based materials in future packaging. In contrast, the low molecular mass fraction might be suitable for the production of biogas and bioethanol. Today, hemicelluloses in process water from CMTP mills are treated in energy demanding waste water treatment plants. The process developed in this project will enable optimal use of different hemicellulose fractions in valuable products, thus leading both to decreased amount of waste, and improved resource efficiency of CTMP mills.

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References

[1] J. Konn, A. Pranovich, B. Holmbom, Dissolution of fibre material in alkaline pretreatment and refining of spruce CTMP, Holzforschung 60 (2006) 32–39.
[2] J. Konn, B. Holmbom, O. Nickull, Chemical reactions in chemimechanical pulping: material balances of wood components in a CTMP process, J. Pulp Paper Sci. 28 (2002) 395–399.
[3] J. Thornton, R. Ekman, B. Holmbom, F. Örså, Polysaccharides dissolved from Norway spruce in thermomechanical pulping and peroxide bleaching, J. Wood Chem. Technol. 14 (1994) 159–175.
[4] A.I. Yaich, U. Edlund, A.-C. Albertsson, Wood hydrolysate barriers: performance controlled via selective recovery, Biomacromolecules 13 (2012) 466–473.
[5] J. Hartman, A.-C. Albertsson, M. Söderqvist Lindblad, J. Sjöberg, Oxygen barrier materials from renewable sources: material properties of softwood hemicellulose-based films, J. Appl. Polym. Sci. 100 (2006) 2985–2991.
[6] M. Gröndahl, L. Eriksson, P. Gatenholm, Material properties of plasticized hardwood xylans for potential application as oxygen barrier films, Biomacromolecules 5 (2004) 1528–1535.
[7] U. Edlund, Y.Z. Ryberg, A.-C. Albertsson, Barrier films from renewable forestry waste, Biomacromolecules 11 (2010) 2532–2538.
[8] I. Gabrielii, P. Gatenholm, W.G. Glasser, R.K. Jain, L. Kenne, Separation, characterization and hydrogel-formation of hemicellulose from aspen wood, Carbohydr. Polym. 43 (2000) 367–374.
[9] S. Willför, K. Sundberg, M. Tenkanen, B. Holmbom, Spruce-derived mannans – a potential raw material for hydrocolloids and novel advanced natural materials, Carbohydr. Polym. 72 (2008) 197–210.
[10] L. Bai, H. Hu, J. Xu, Influence of configuration and molecular weight of hemicelluloses on their paper-strengthening effects, Carbohydr. Polym. 88 (2012) 1258–1263.
[11] L. Puro, M. Kallioinen, M. Mänttäri, M. Nyström, Evaluation of behavior and fouling potential of wood extractives in ultrafiltration of pulp and paper mill process water, J. Membr. Sci. 368 (2011) 150–158.
[12] M. Al Manasrah, M. Kallioinen, H. Ilvesniemi, M. Mänttäri, Recovery of galactoglucomannan from wood hydrolysate using regenerated cellulose ultrafiltration membranes, Bioresour. Technol. 114 (2012) 375–381.
[13] N. Westerberg, H. Sunner, M. Helander, G. Henriksson, M. Lawoko, A. Rasmuson, Separation of galactoglucomannans, lignin, and lignin-carbohydrate complexes from hot-water-extracted Norway spruce by cross-flow filtration and adsorption chromatography, Bioresources 7 (2012) 4501–4516.

[14] A. Sundberg, S. Willför, P. Rehn, B. Holmbom, Can water-soluble O-acetyl-galactoglucomannans be isolated in large-scale from TMP?, in: Proc. 12th Int. Symposium on Wood and Pulping Chemistry, University of Wisconsin-Madison, vol. 2, 2003.
[15] S. Willför, P. Rehn, A. Sundberg, K. Sundberg, B. Holmbom, Recovery of water-soluble acetylgalactoglucomannans from mechanical pulp of spruce, Tappi J. 2 (2003) 27–32.
[16] H. Krawczyk, A.-S. Jönsson, Separation of dispersed substances and galactoglucomannan in thermomechanical pulp process water by microfiltration, Sep. Purif. Technol. 79 (2011) 43–49.
[17] T. Persson, A.-K. Nordin, G. Zacchi, A.-S. Jönsson, Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce, Appl. Biochem. Biotechnol. 137 (2007) 741–752.
[18] T. Persson, H. Krawczyk, A.-K. Nordin, A.-S. Jönsson, Fractionation of process water in thermomechanical pulp mills, Bioresour. Technol. 101 (2010) 3884–3892.
[19] L. Puro, M. Kallioinen, M. Mänttäri, G. Natarajan, D.C. Cameron, M. Nyström, Performance of RC and PES ultrafiltration membranes in filtration of pulp mill process waters, Desalination 264 (2010) 249–255.
[20] P. Ramamurthy, R. Poole, J.G. Dorica, Fouling of ultrafiltration membranes during treatment of CTMP screw press filtrates, J. Pulp Paper Sci. 21 (1995) J50–J54.
[21] T. Persson, A.-S. Jönsson, Isolation of hemicelluloses by ultrafiltration of thermomechanical pulp mill process water – influence of operating conditions, Chem. Eng. Res. Des. 88 (2010) 1548–1554.
[22] C.-H. Ko, C. Fan, Enhanced chemical oxygen demand removal and flux reduction in pulp and paper wastewater treatment using laccase-polymerized membrane filtration, J. Hazard. Mater. 181 (2010) 763–770.
[23] D. Areskogh, J. Li, G. Gellerstedt, G. Henriksson, Investigation of the molecular weight increase of commercial lignosulfonates by laccase catalysis, Biomacromolecules 11 (2010) 904–910.
[24] G. Henriksson, D. Areskogh, P. Oinonen, A method to increase the molecular weight of wood mannans and xylans comprising aromatic moieties, Patent Application PCT/WO2012071004, 2012.
[25] R. Ruiz, T. Ehrman, Laboratory analytical procedure LAP-014: dilute acid hydrolysis procedure for determination of total sugars in the liquid fraction of process samples, NREL, Midwest Research Institute for the Department of Energy, USA, 1996.
[26] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Laboratory analytical procedure (LAP): determination of structural carbohydrates and lignin in biomass, NREL, Midwest Research Institute for the Department of Energy, USA, 2008.
[27] E. Sjöström, Wood Chemistry – Fundamentals and Applications, Academic Press, 1993.
[28] J. Käyhkö, The influence of process conditions on the deresination efficiency in mechanical pulp washing, PhD thesis, Lappeenranta University of Technology, Department of Chemical Technology, 2002.
[29] M. Lawoko, G. Henriksson, G. Gellerstedt, Characterization of lignin-carbohydrate complexes (LCCs) of spruce wood (*Picea abies* L.) isolated with two methods, Holzforschung 60 (2006) 156–161.
[30] C. Xu, S. Willför, P. Holmlund, B. Holmbom, Rheological properties of water-soluble spruce O-acetyl galactoglucomannans, Carbohydr. Polym. 75 (2009) 498–504.

Paper IV

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Membrane performance during ultrafiltration of a high-viscosity solution containing hemicelluloses from wheat bran

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ABSTRACT

Hemicelluloses isolated from agricultural residues have the potential to replace fossil-based materials in high-value-added applications, provided that cost-efficient isolation processes are developed. In this study, a feed solution containing hemicelluloses extracted from wheat bran with a particular high viscosity was used to study the performance of ultrafiltration for hemicellulose isolation at various operating conditions. The operating parameters affected the flux significantly, but had no influence on the retention of the membrane. The flux was doubled by: (i) increasing the cross-flow velocity from 2 to 5 m/s, (ii) increasing the feed temperature from 60 to 80 °C and (iii) decreasing the concentration of the solution by half. The flux increase could mainly be attributed to a decrease in the apparent viscosity of the feed solution. This indicates that low feed viscosity is the key to good membrane performance. The limiting flux during ultrafiltration was reached at the low transmembrane pressure of 0.8 bar, even when the cross-flow velocity and feed temperature were as high as 5 m/s and 80 °C, respectively. Low transmembrane pressure is thus preferable during ultrafiltration of solutions similar to that used in the present investigation. The results of this study suggest that ultrafiltration could be a suitable method for the isolation of hemicelluloses from high-viscosity solutions. However, as the operating parameters affect the membrane performance significantly, they must be chosen with care to make the process cost-efficient.

1. Introduction

Wheat bran, like all lignocellulosic materials, is composed mostly of cellulose, hemicelluloses and lignin. The hemicelluloses consist mainly of arabinoxylan: a heteropolysaccharide composed of a xylan backbone with arabinofuranosyl side groups [1]. It has been shown in several studies that arabinoxylan and other hemicelluloses in lignocellulosic material have interesting properties as a feedstock for the manufacture of products such as oxygen barrier films for food packaging materials [2–5]. More recently, the use of hemicelluloses for oxygen barrier films has attracted much attention in the packaging industry, as the material used today for producing such films, ethylene vinyl alcohol, is made from fossil resources.

In order to make use of hemicelluloses, they must first be extracted from the plant material and then separated from the resulting solution by chemical and/or mechanical methods. One extraction process employing chemical treatment is the alkali extraction method. Several variations of this method have been suggested for wheat bran [6–11], and it has been shown that hemicelluloses with large molecular mass can be extracted at reasonably good yields. Hemicelluloses can also be separated using membrane ultrafiltration, as has been shown in several studies using pulp mill process water as a hemicellulose source [12–15]. Furthermore, some research reports on the application of ultrafiltration to solutions obtained after hemicellulose extraction from lignocellulosic material such as wheat bran [10,16,17] and barley husks [18]. These studies confirmed the suitability of ultrafiltration for hemicellulose isolation; however, no detailed investigations were made of the effects of the operating parameters on the membrane performance.

Wheat bran probably has the highest potential of all lignocellulosic materials as a hemicellulose source for a commercial extraction process as it is available in sufficiently large quantities. However, the hemicellulose solution obtained after alkali extraction of wheat bran is of particularly high viscosity due to the structural characteristics of the macromolecules in this kind of biomass. High viscosity of the feed solution is associated with an increase in the frictional pressure drop along a tubular membrane during ultrafiltration. This pressure drop can decrease the driving force during filtration, leading to poor membrane performance [19]. In order to realize a cost-efficient process knowledge is required on the relations between operating parameters and membrane performance during ultrafiltration.

In this study, the influence of various operating parameters on membrane performance during ultrafiltration of a hemicellulose

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solution with particularly high viscosity was investigated. The solution used was obtained by alkali extraction of hemicelluloses from wheat bran. Operating parameters taken into account in the investigation were the cross-flow velocity, the transmembrane pressure, the temperature and the concentration of the solution. The results obtained increase our understanding of how hemicelluloses can be isolated most cost-efficiently from viscous solutions, and will help in replacing fossil-based barrier films in future food packaging materials.

2. Materials and methods

2.1. Hemicellulose solution

The hemicellulose solution used in this investigation was obtained by extraction of hemicelluloses from wheat bran using an alkali extraction method. The structure of the biomass was broken down by enzymatic treatment, during which the starch in the wheat bran is degraded and removed. Sodium hydroxide (NaOH) was then used to extract the hemicelluloses from the fibers, resulting in the hemicelluloses-rich solution used in this investigation.

2.2. Equipment

2.2.1. Membrane

A tubular ceramic membrane made of α-Al_2O_3 with a TiO_2 top layer was used (Atech Innovations GmbH, Gladbeck, Germany). The specifications of the membrane are given in Table 1. The sealing material on the end caps of the membrane was polytetrafluoroethylene (PTFE) instead of the standard material polyurethane. PTFE was chosen because of its higher resistance to high pH in combination with high temperature.

2.2.2. Experimental setup

A schematic of the experimental setup used in this work is shown in Fig. 1. The most important components are two 200-L tanks, an M1 module (Atech innovations) in which the ceramic membrane was installed, and a circulation pump (NB32/25-20, ABS Pump Production, Mölndal, Sweden). Tank 1 was only used during cleaning and start-up, while Tank 2 served as the feed tank during ultrafiltration of the hemicellulose solution. The transmembrane pressure during ultrafiltration was controlled by manually adjusting valves installed on the permeate and the retentate side of the membrane. The cross-flow velocity was controlled by the pump speed using a frequency converter (CDA3000, Lust Antriebstechnik GmbH, Germany). The transmembrane pressure, P_t, was calculated from the relation:

$$P_t = \frac{P_{\mathrm{in}} + P_{\mathrm{out}}}{2} - P_p \qquad (1)$$

where P_{in}, P_{out} and P_p are the pressures at the inlet, the outlet and on the permeate side of the membrane, respectively. The frictional pressure drop was calculated as the difference between the inlet and outlet pressure.

Table 1
Specifications of the membrane used in the experiments.

Overall length	1000 mm
Outer diameter	25.4 mm
Number of channels	7
Diameter of channels	6 mm
Filtration area	0.132 m^2
Molecular weight cut-off	10 kDa
Sealing material	PTFE

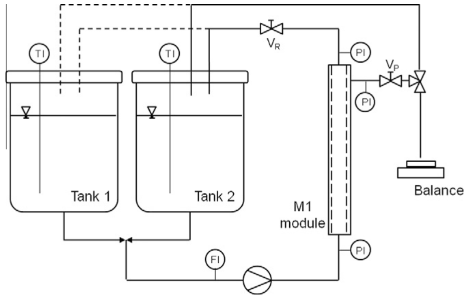

Fig. 1. Schematic of the experimental setup.

2.2.3. Instrumentation

The experimental setup was equipped with three pressure transmitters (dTrans p02, Jumo AB, Helsingborg, Sweden): one at the inlet, one at the outlet and one on the permeate side of the membrane. A volume flow meter (Fischer&Porter Co. Ltd., Göttingen, Germany) was used to measure the feed flow, and an electronic balance (PL6001-S, Mettler-Toledo Inc., Columbus, OH) was used to determine the permeate flux. A Pt100 element was inserted into the feed tank for temperature measurements. All data from the measuring devices were continuously recorded using LabView software (National Instruments Co, Austin, TX).

2.3. Experimental procedure

2.3.1. Membrane cleaning

The membrane was cleaned for 1 h before and after the experimental runs with a 0.5 wt% solution of the alkali cleaning agent Ultrasil 10 (Ecolab AB, Älvsjö, Sweden). The temperature during cleaning was 50 °C. After cleaning, the membrane was rinsed thoroughly with deionized water and the pure water flux was measured at 30 °C and a transmembrane pressure of 1 bar.

2.3.2. Start-up procedure

Before performing the experimental studies a start-up procedure was performed, involving both feed tanks. First, Tank 1 was connected to the circulation loop and filled with a 0.1 M NaOH solution, which was subsequently circulated through the system for 12 h. This was done to prevent a sudden change in pH upon introducing the hemicelluloses solution, thus preventing possible precipitation of certain substances in the initial stages of the experiments. During circulation at a cross-flow velocity of 4 m/s and a transmembrane pressure of 1 bar, the NaOH solution was heated to 60 °C. About 80 L of the hemicellulose solution was then pumped into Tank 2 and heated to the same temperature as the solution in Tank 1. During heating, the hemicellulose solution in Tank 2 was mixed with an external mono pump (SH40R8/C, Mono Pumps Ltd., London, UK). The feed was switched from Tank 1 to Tank 2, and the NaOH solution was displaced from the system. The hemicellulose solution was circulated with the permeate valve closed and a cross-flow velocity of 4 m/s. In order to investigate different operating conditions, the temperature and the cross-flow velocity were adjusted first, and then the permeate valve was opened in order to adjust the transmembrane pressure.

2.3.3. Study of operating parameters

The permeate and retentate were returned to Tank 2 during the study of transmembrane pressure and cross-flow velocity. The study was performed at a temperature of 80 °C, and then at 60 °C.

Between the studies at the two temperatures, the membrane was cleaned and the solution was replaced with fresh solution. The influence of the transmembrane pressure on membrane performance was investigated at a constant cross-flow velocity of 5 m/s. During this investigation the permeate valve was opened very carefully in order to slowly increase the transmembrane pressure from 0 to 1.5 bar. The influence of the cross-flow velocity on membrane performance was then investigated. The transmembrane pressure was maintained at 1.5 bar, and the cross-flow velocity was decreased stepwise (5, 4, 3, 2 m/s). The cross-flow velocity was then increased stepwise to the initial value in order to evaluate the reversibility of membrane fouling. The flux was recorded at each velocity for 30 min and samples were taken from the permeate and feed. The entire investigation took about 6 h at each temperature.

In order to study the influence of concentration on membrane performance, the hemicellulose solution was diluted 1:1 with 0.1 M NaOH solution. The diluted solution was subsequently concentrated by withdrawing permeate to a volume reduction (VR) of 50%. VR is defined as the ratio of the total volume of permeate withdrawn to the initial volume of the feed. Constant operating parameters were used in the concentration study: a transmembrane pressure of 1.5 bar, a cross-flow velocity of 5 m/s and a temperature of 80 °C.

2.4. Component analysis

2.4.1. Total solids, ash and sodium hydroxide

Duplicate samples were dried in weighed porcelain crucibles for 24 h in an oven at 105 °C. The content of total solids was determined from the weight of the residue after cooling to room temperature in a desiccator.

The ash content was determined by heating the dried samples further to 575 °C, and maintaining this temperature for 3 h. The ash content was calculated from the weight of the residue after cooling to room temperature in a desiccator.

It was assumed that ash in the samples was completely derived from the NaOH added during alkali extraction. In order to determine the content of NaOH, a correction must be made, since at high temperature NaOH forms Na_2O and water, according to the following chemical reaction [20]:

$$2NaOH \rightarrow Na_2O + H_2O \tag{2}$$

The mass of NaOH in a sample decreases during ash analysis because the water formed in the reaction evaporates. The correction factor of 1.29 used to account for this weight loss was derived from the stoichiometry of the chemical reaction and verified experimentally by measuring the weight loss of a known amount of pure NaOH during ignition at 575 °C.

2.4.2. Monomeric sugars

Monomeric sugars were measured after acid hydrolysis using high-performance anion-exchange chromatography coupled with pulsed amperometric detection in an ICS-3000 chromatography system (Dionex Corp., Sunnyvale, CA). The system was equipped with a Carbo Pac PA1 analytical column. A solution of 200 mM NaOH dissolved in 170 mM sodium acetate was used to clean the column. Deionized water was used as eluent during the analysis. The monomeric sugars D-glucose, D-galactose, D-mannose, D-xylose and L-arabinose (Fluka Chemie AG, Buchs, Switzerland) were used as standards. Acid hydrolysis was performed according to the standardized NREL method [21].

2.4.3. Acid-insoluble solids and acid-soluble lignin

The content of acid-insoluble solids was determined after acid hydrolysis (NREL method). Precipitates were retained in a weighed filter crucible with a maximal pore size of 16 μm (Schott AG, Mainz, Germany), and then dried for 24 h in an oven at 105 °C. The content of acid-insoluble solids was then determined as the weight of the residue after cooling to room temperature in a desiccator.

The content of acid-soluble lignin was determined in the solution passing through the crucible filter by measuring the UV absorbance at a wavelength of 320 nm in a spectrophotometer (UV-160, Shimadzu Corp., Kyoto, Japan). An extinction coefficient similar to that of corn stover, of 30 L/g cm, was used [22].

2.4.4. Molecular mass distribution of hemicelluloses

The molecular mass distribution of hemicelluloses was determined by size exclusion chromatography using a Waters 600E chromatography system (Waters, Milford, MA) equipped with a refractive index detector (model 410, Waters). The analytical column was packed with 30 cm of Superdex 30 and 30 cm of Superdex 200 (GE Healthcare, Uppsala, Sweden). A 125 mM NaOH solution was used as eluent at a flow rate of 1 mL/min. The system was calibrated with polyethylene standards with peak molecular masses of 0.4, 4, 10 (Merck Schuchardt OHG, Hohenbrunn, Germany) and 40 kg/mol (Serva Electrophoresis GmbH, Heidelberg, Germany).

2.4.5. Viscosity

Viscosity measurements were performed in a Malvern Kinexus Pro rotational rheometer with a torque range of 0.05 μNm to 200 mNm. A cup-and-bob geometry was used. The system allowed the temperature of the sample to be kept constant during the measurements. The apparent viscosity was measured at a temperature of 60 °C in the shear rate range 1–100 s^{-1}, unless otherwise stated.

3. Results and discussion

The solution used in this investigation contained hemicelluloses extracted from wheat bran by alkali extraction. This solution is a complex mixture from which the hemicelluloses must be isolated. Knowledge about the chemical composition and the physical properties of the solution is necessary in order to be able to design an efficient ultrafiltration process. Thus, the solution was first characterized by determining its composition, and physical properties and their dependency on temperature and pH. Based on the outcome of this characterization, ultrafiltration experiments were performed in the second part of the investigation.

3.1. Characterization of the hemicellulose solution

3.1.1. Composition

The composition of the hemicellulose solution is given in Table 2. The content of total solids in the solution was about 52 g/L of which NaOH, hemicelluloses and acid-insoluble solids accounted for the largest fractions. The high amount of NaOH is due to the large addition of this chemical in the procedure used to extract hemicelluloses from wheat bran. Hemicelluloses were mainly arabinoxylans with a ratio of the monosaccharides xylose:arabinose of 2.3:1. This ratio was somewhat higher than the ratios of 1.3:1 to 2:1 reported for arabinoxylan extracted from wheat bran by other researchers [7,8,10,17], and can be attributed to differences in the alkali extraction method and the raw material. The average molecular mass of hemicelluloses in the solution was about 90 kg/mol. The solids in the solution, presented as acid-insoluble solids in Table 2, were assumed to be mainly lignin and proteins. In native wheat bran, lignin and proteins account for about 3–9 and 14–18% of the vegetable matter, respectively [7,8,10,11,17]. It is thus likely that fractions of these components are extracted during alkali treatment of the raw material.

Table 2
Characterization of the hemicellulose solution used in this investigation.

Total composition	
Total solids (g/L)	51.7
NaOH (g/L)	39.5
Hemicelluloses (g/L)	7.7
Acid-insoluble solids (g/L)	3.2
Acid-soluble lignin (g/L)	0.3
Hemicelluloses	
Arabinose (g/L)	1.85
Galactose (g/L)	0.13
Glucose (g/L)	1.40
Xylose (g/L)	4.35
Ave. Molecular mass (kDa)	90
Physical properties	
pH	13
Viscosity [a](mPa s)	6.7
Density (kg/m3)	1019

[a] Measured at 60 °C at a shear rate of 100 s^{-1}.

The physical properties of the solution are of particular importance, since they influence the performance of membrane filtration. The viscosity of the solution was about 14 times the viscosity of water at 60 °C (Table 2). Moreover, the solution was very alkaline. Both the high viscosity and extreme alkalinity were the reason for choosing a tubular ceramic membrane for ultrafiltration in this investigation. Compared to their polymeric competitors, ceramic membranes are more resistant to extreme conditions (pH, temperature) and the tubular design provides large feed channels, resulting in lower pressure drops. The latter is of particular importance for highly viscous solutions.

3.1.2. Solution viscosity at various temperatures and pH

High viscosity of a solution generally leads to an increase in the pressure drop along the membrane module and a decrease in the mass transfer coefficient [23,24]. Both are undesirable because of their negative effects on the energy requirement and membrane performance. Therefore, highly viscous feed solutions should be avoided, if possible, during ultrafiltration. Viscosity is dependent on factors such as temperature and pH; thus, studying the rheological behavior of the hemicellulose solution while varying these factors can provide valuable information on the optimal operating conditions for ultrafiltration. In this investigation, the pH of the solution was adjusted by aeration with carbon dioxide, which dissolves forming carbonic acid. In addition to the untreated solution (pH 13), two solutions with final pH of 10 and 8 were obtained using this method.

During viscosity measurements the solution showed shear-thinning behavior, that is, increasing shear rate led to decreased viscosity (Fig. 2a). This behavior may be explained by steric interactions between macromolecules in solution at low shear rates, resulting in high viscosity. When the shear rate is increased the molecules start to align in the direction of the shearing force, which decreases the solution's viscosity. At high shear rates, only a slight decrease in viscosity was observed. This may be due to the already almost perfect alignment of the molecules.

As expected, the temperature and pH of the solution had a significant influence on the viscosity. At 50 °C and a shear rate of 100 s^{-1}, the apparent viscosity was 8.5 mPa s, which is more than double the value obtained at 80 °C (Fig. 2a). When the pH of the solution was decreased by dissolution of carbon dioxide, the viscosity increased significantly (Fig. 2b). This behavior can be explained by lower electrostatic repulsion between the macromolecules, which occur, as the surface charge of the macromolecules changes with pH.

The characterization of the hemicellulose solution provided valuable information that was used to design the ultrafiltration experiments. As shown in Fig. 2, high temperature and high pH decreased the apparent viscosity of the solution. As a lower viscosity is associated with better membrane performance, the ultrafiltration experiments were performed with a hemicellulose solution with high alkalinity (pH 13) at high temperature (80 °C). In addition, some experiments were performed at a lower temperature of 60 °C, as a reference case. The operating parameters taken into consideration in the ultrafiltration studies were the transmembrane pressure, the cross-flow velocity and the concentration of the hemicellulose solution.

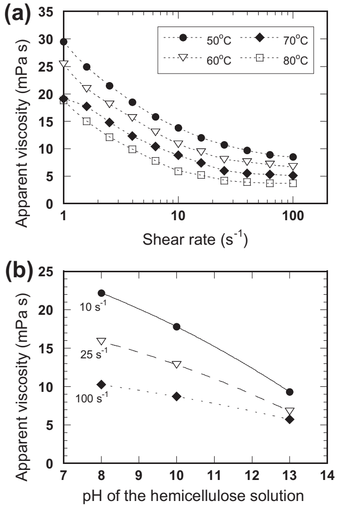

Fig. 2. Influence of (a) temperature and (b) pH on the apparent viscosity of the hemicellulose solution at various shear rates.

3.2. Influence of transmembrane pressure on membrane performance

During the start-up of the ultrafiltration procedure, the transmembrane pressure was increased gradually from zero to the operating pressure of 1.5 bar. The increase in flux during start-up for the experiments performed at 60 and 80 °C, is shown in Fig. 3. The cross-flow velocity was 5 m/s in both cases.

At both temperatures, the flux initially increased linearly with pressure, started to level-off at 0.5 bar, and then remained more

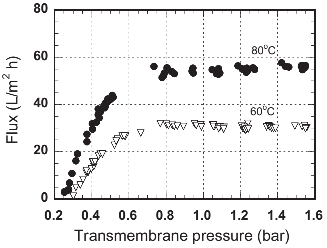

Fig. 3. Influence of the transmembrane pressure on flux during ultrafiltration of the hemicellulose solution.

or less constant above a transmembrane pressure of 0.8 bar (see Fig. 3). This non-linear behavior of the flux with TMP is often observed during ultrafiltration and can be associated with the formation of a gel layer on the membrane surface [23]. At pressures above 0.8 bar the thickness, and thus the resistance, of the gel layer increased at about the same rate as the driving force for filtration; thus, the flux remained essentially constant. Furthermore, the temperature was found to have a considerable influence on the flux. At 80 °C the maximal flux was about 58 L/m^2 h; i.e. almost twice that at 60 °C. These significant differences in the flux are in agreement with the results of the viscosity measurements in Fig. 2a, in which it can be seen that the solution has a much higher viscosity at 60 °C than at 80 °C.

The operating transmembrane pressure in ultrafiltration applications usually ranges between 2 and 10 bar, depending on the solution properties. However, such high transmembrane pressures are not recommended in the present case, since the limiting flux was reached at a pressure of only 0.8 bar. According to Bacchin et al., the limiting flux may correspond to the flux at which the filtration capacity of the membrane is saturated due to fouling [25]. Thus, operating ultrafiltration above the limiting pressure is not only a waste of energy, it also increases the need and frequency of cleaning.

3.3. Influence of cross-flow velocity on membrane performance

The cross-flow velocity is one of the dominating factors affecting membrane performance during ultrafiltration. High cross-flow velocity is generally beneficial, since it increases the mass transfer coefficient [23]. However, high cross-flow velocity also increases the frictional pressure drop along the membrane module, particularly when solutions of high viscosity are treated. As a result, the inlet transmembrane pressure can be high and fouling can occur, especially in the first part of the membrane.

Fig. 4 shows the influence of the cross-flow velocity on flux and frictional pressure drop along the membrane during ultrafiltration. The initial cross-flow velocity was 5 m/s, it was then decreased stepwise to 2 m/s, and was finally increased to the initial value. The membrane flux and frictional pressure drop were markedly affected by the cross-flow velocity at both temperatures, as can be seen in Fig. 4. As the cross-flow velocity was decreased, the flux decreased from 63 to 30 L/m^2 h at a temperature of 80 °C, and from 33 to 14 L/m^2 h at 60 °C. Although the cross-flow velocity had a significant effect on flux and pressure drop, the retention of the membrane was unaffected. The retention of hemicelluloses, total solids and NaOH over the entire range of cross-flow velocity was 96%, 18% and 8%, respectively.

In general, the flux tends to remain constant, or decline due to membrane fouling, under constant operating conditions. This was not the case in the present investigation, as can be seen in Fig. 4a by comparing the flux at the same cross-flow velocity, at the start and the end of the experiment. Instead, a flux increase of up to 28% at 80 °C and up to 18% at 60 °C was observed. A possible explanation of this finding may be that the viscosity of the solution changed during the experiments due to the elevated temperature and shear stress. A separate experiment was therefore performed to substantiate this hypothesis. Hemicellulose solution was stored in an oven at 80 °C and the apparent viscosity of samples taken after 18, 26, 52 and 98 h of storage was measured. As can be seen in Fig. 5, the viscosity of the solution decreased markedly with storage duration. It is likely that breakage of chemical bonds within macromolecules (e.g. in hemicelluloses, lignin and proteins) in the solution caused this viscosity decline. From these results it was concluded that the differences in the initial and final fluxes at constant cross-flow velocity can be attributed to changes in the viscosity of the solution. The degradation of macromolecules will probably be more pronounced at 80 °C than at 60 °C, which explains the larger difference between initial and final flux at the higher temperature.

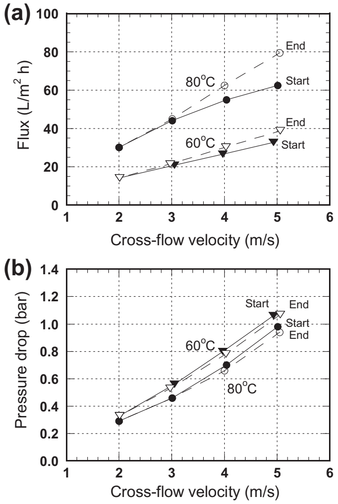

Fig. 4. Influence of the cross-flow velocity on (a) flux and (b) frictional pressure drop during ultrafiltration of hemicellulose solution.

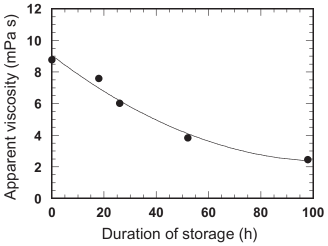

Fig. 5. Influence of the duration of storage at 80 °C on the apparent viscosity of the hemicellulose solution at a shear rate of 100 s^{-1}.

3.4. Influence of concentration on membrane performance

In order to obtain hemicelluloses at high concentration and purity in a potential industrial process, water and low-molecular-weight components must be removed, as far as possible, from the hemicellulose solution. During such a concentration process the membrane performance will certainly be affected by the increasing concentration of hemicelluloses in the feed. In this investigation, the influence of feed concentration on membrane performance was studied by diluting the feed solution with a 0.1 M NaOH solution at the ratio 1:1. Using an alkaline solution instead of deionized water for dilution had the advantage that the pH of the feed solution remained constant, which prevented an increase in the solution viscosity during dilution, due to a change of pH (see Fig. 2b). After dilution the solution was concentrated under constant operating conditions by withdrawing permeate from the system until the initial feed concentration was reached (VR 50%). This procedure allowed us, firstly, to follow the flux during a concentration process and, secondly, to draw conclusions on membrane fouling by comparing the flux before dilution with NaOH solution with the flux after concentration to a VR of 50%.

The initial flux after dilution was 146 L/m^2 h, thus significantly higher than the flux prior to dilution, which was 80 L/m^2 h. This difference can be explained by the fact that the viscosity of the solution is highly dependent on the concentration. For example, the viscosity of the feed at 80 °C and a shear rate of 100 s^{-1} was 2.5 mPa s before dilution, but only 1.4 mPa s after addition of the NaOH solution. The strong influence of the feed concentration on membrane performance can also be seen in Fig. 6, in which the flux is shown during the concentration process. As expected, the flux decreased markedly with increasing VR. It is interesting to note that at a VR of 50%, at which the feed concentration was about the same as in the feed prior to dilution, the flux was also the same. This observation indicates that the membrane was not fouled during the study. This reasoning was confirmed by comparing the pure water flux after cleaning, before and after performance of the experimental study. The pure water flux after concentration was about 92% of the initial pure water flux. A decline in the pure water flux of this magnitude should not be attributed to fouling, and it is not uncommon when using a membrane for the first time [26].

The results of this investigation showed that, the operating parameters have a considerable influence on membrane performance during ultrafiltration of a highly viscous hemicellulose solution. These findings show that low transmembrane pressure, high cross-flow velocity and high temperature should be used to obtain the highest possible flux. However, these operating conditions are not optimal with respect to the energy demand, since the power required for pumping and heating increases as the cross-flow velocity and the temperature are increased.

3.5. Effect of operating parameters on energy requirement for recirculation

In most ultrafiltration processes, the largest part of the energy requirement is attributed to recirculation of the retentate [26]. The electrical power required for recirculation is obviously dependent on the volume recirculated and the properties of the solution, such as the viscosity and density. Thus, besides flux and retention, the operating parameters used for ultrafiltration also influence the energy required for recirculation, which must be considered when choosing the optimal operating conditions for the ultrafiltration process.

The energy requirement per unit volume of permeate in the recirculation pumps can be calculated using Eq. (3) [26]:

$$W = \frac{\Delta P_f \cdot Q}{\eta \cdot (J \cdot A)} \tag{3}$$

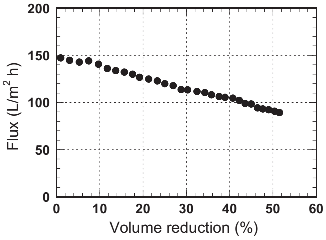

Fig. 6. Flux after dilution and during subsequent concentration of the hemicellulose solution to a volume reduction of 50%.

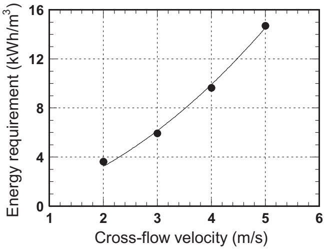

Fig. 7. Energy requirement per m^3 of permeate in the recirculation pumps with increasing cross-flow velocity with a feed temperature of 80 °C.

where ΔP_f is the frictional pressure drop along the membrane module, Q is the feed flow, η is the pump efficiency, J is the flux and A is the filtration area of the membrane. In the present case the pump efficiency was assumed to be 0.8.

As can be seen from Eq. (3), the operating conditions that give a high flux during ultrafiltration, should also be beneficial with respect to the energy requirement per unit volume of permeate, as increasing the flux decreases the energy requirement. This suggests that the highest possible transmembrane pressure should be used during ultrafiltration, which was determined to be about 0.8 bar in the present investigation (see Fig. 3). However, this reasoning does not apply to the cross-flow velocity. Although the flux is higher at high cross-flow velocity, the energy required by the recirculation pumps is also higher (Fig. 7). For example, at 80 °C, the energy requirement at 5 m/s is 15 kW h/m^3, which is about four times higher than at 2 m/s (3.6 kW h/m^3). Obviously, this can be explained by the fact that the frictional pressure drop in Eq. (3) increases more significantly than the membrane flux when the cross-flow velocity is increased.

4. Conclusions

The hemicellulose solution used in this investigation was produced using alkali extraction of hemicelluloses from wheat bran. The performance of ultrafiltration for hemicellulose isolation from this solution, with a particularly high viscosity, was studied using a ceramic tubular membrane (cut-off 10 kDa). An acceptably high flux (up to 62 L/m^2 h), high hemicellulose retention (96%) and no significant fouling of the membrane were observed; from which it was concluded that ultrafiltration is a promising technique for hemicellulose isolation from highly viscous solutions. The operating parameters were found to affect the membrane flux significantly, but had no influence on the membrane retention. The limiting flux was reached at the low transmembrane pressure of 0.8 bar, even with a high cross-flow velocity (5 m/s) and high temperatures (60 and 80 °C). Decreasing the cross-flow velocity from 5 to 2 m/s was found to reduce the flux by half (from 62 to 30 L/m^2 h). Furthermore, the membrane flux was found to decrease significantly with increasing feed concentration. These results demonstrate that the membrane performance is strongly associated with the viscosity of the feed solution, and it was concluded that decreasing the feed viscosity is the key to a cost-efficient ultrafiltration process. The present work focused on identifying the operating parameters with the greatest influence on ultrafiltration of a highly viscous hemicellulose solution. In order to optimize the hemicellulose isolation process, a more detailed investigation is required, which should include an economic evaluation of the process. In such a study, the average flux during concentration should be used in the calculations, as it is likely that, at low velocity, the flux will decrease more rapidly with increasing VR than at high cross-flow velocity. An economic evaluation will be included in a future investigation.

Acknowledgment

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References

[1] A. Ebringerová, T. Heinze, Xylan and xylan derivatives – biopolymers with valuable properties 1, Macromol. Rapid Commun. 21 (2000) 542–556.

[2] M. Gröndahl, L. Eriksson, P. Gatenholm, Material properties of plasticized hardwood xylans for potential application as oxygen barrier films, Biomacromolecules 5 (2004) 1528–1535.

[3] N.M.L. Hansen, D. Plackett, Sustainable films and coatings from hemicelluloses: a review, Biomacromolecules 9 (2008) 1493–1505.

[4] J. Hartman, A.-C. Albertsson, M. Söderqvist Lindblad, J. Sjöberg, Oxygen barrier materials from renewable sources: material properties of softwood hemicellulose-based films, J. Appl. Polym. Sci. 100 (2006) 2985–2991.

[5] A. Höije, M. Gröndahl, K. Tømmeraas, P. Gatenholm, Isolation and characterization of physicochemical and material properties of arabinoxylans from barley husks, Carbohydr. Polym. 61 (2005) 266–275.

[6] G. Annison, M. Choct, N.W. Cheetham, Analysis of wheat arabinoxylans from a large-scale isolation, Carbohydr. Polym. 19 (1992) 151–159.

[7] M. Bataillon, P. Mathaly, A.P. Nunes Cardinali, F. Duchiron, Extraction and purification of arabinoxylan from destarched wheat bran in a pilot scale, Ind. Crops Prod. 8 (1998) 37–43.

[8] M.E.F. Bergmans, G. Beldman, H. Gruppen, A.G.J. Voragen, Optimisation of the selective extraction of (glucurono)arabinoxylans from wheat bran: use of barium and calcium hydroxide solution at elevated temperatures, J. Cereal. Sci. 23 (1996) 235–245.

[9] M.S. DuPont, R.R. Selvendran, Hemicellulosic polymers from the cell walls of beeswing wheat bran: Part 1, polymers solubilised by alkali at 2°, Carbohydr. Res. 163 (1987) 99–113.

[10] J. Hollmann, M.G. Lindhauer, Pilot-scale isolation of glucuronoarabinoxylans from wheat bran, Carbohydr. Polym. 59 (2005) 225–230.

[11] S. Zhou, X. Liu, Y. Guo, Q. Wang, D. Peng, L. Cao, Comparison of the immunological activity of arabinoxylans from wheat bran with alkali and xylanase-aided extraction, Carbohydr. Polym. 81 (2010) 784–789.

[12] T. Persson, A.-K. Nordin, G. Zacchi, A.-S. Jönsson, Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce, Appl. Biochem. Biotechnol. 137 (2007) 741–752.

[13] T. Persson, A.-S. Jönsson, Fouling of ultrafiltration membranes during isolation of hemicelluloses in the forest industry, Schol. Res. Exch. Eng. (2009), doi:10.3814/2009/624012.

[14] T. Persson, A.-S. Jönsson, Isolation of hemicelluloses by ultrafiltration of thermomechanical pulp mill process water – influence of operating conditions, Chem. Eng. Res. Des. 88 (2010) 1548–1554.

[15] R. Schlesinger, G. Götzinger, H. Sixta, A. Friedl, M. Harasek, Evaluation of alkali resistant nanofiltration membranes for the separation of hemicellulose from concentrated alkaline process liquors, Desalination 192 (2006) 303–314.

[16] J. Jorda, P. Marechal, L. Rigal, P.Y. Pontalier, Biopolymer purification by ultrafiltration, Desalination 148 (2002) 187–191.

[17] R. Zeitoun, P.Y. Pontalier, P. Marechal, L. Rigal, Twin-screw extrusion for hemicellulose recovery: influence on extract purity and purification performance, Bioresour. Technol. 101 (2010) 9348–9354.

[18] H. Krawczyk, T. Persson, A. Andersson, A.-S. Jönsson, Isolation of hemicelluloses from barley husks, Food Bioprod. Process. 86 (2008) 31–36.

[19] A.-K. Nordin, A.-S. Jönsson, Optimisation of membrane area and energy requirement in tubular membrane modules, Chem. Eng. Process. 47 (2008) 1090–1097.

[20] V.P. Yurkinskii, E.G. Firsova, S.A. Proskura, Thermal dissociation of sodium hydroxide upon evacuation, Russ. J. Appl. Chem. 78 (2005) 360–362.

[21] R. Ruiz, T. Ehrman, Laboratory analytical procedure LAP-014: dilute acid hydrolysis procedure for determination of total sugars in the liquid fraction of process samples, NREL, Midwest Research Institute for the Department of Energy, USA, 1996.

[22] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Laboratory analytical procedure (LAP): determination of structural carbohydrates and lignin in biomass, NREL, Midwest Research Institute for the Department of Energy, USA, 2008.

[23] W.F. Blatt, A. Dravid, A.S. Michaels, L. Nelsen, Solute polarization and cake formation in membrane ultrafiltration: causes, consequences, and control techniques, in: J.E. Flinn (Ed.), Membrane Science and Technology, Plenum Press, New York, 1970, pp. 47–97.

[24] M. Pritchard, J.A. Howell, R.W. Field, The ultrafiltration of viscous fluids, J. Membr. Sci. 102 (1995) 223–235.

[25] P. Bacchin, P. Aimar, R.W. Field, Critical sustainable fluxes: theoryexperiments and applications, J. Membr. Sci. 281 (2006) 42–69.

[26] M. Cheryan, Ultrafiltration and Microfiltration Handbook, second ed., Technomic Publishing Co. Inc., Lancaster, 1998.

Paper V

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Impact of prefiltration on membrane performance during isolation of hemicelluloses extracted from wheat bran

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ABSTRACT

Hemicelluloses extracted from wheat bran have to be separated from impurities in order to obtain a valuable product at high concentration and purity. A previous investigation showed that separation by ultrafiltration is possible, but the flux was low due to the high viscosity of the solution and the presence of gel-forming substances in the solution. In this investigation the influence of prefiltration on solution viscosity and ultrafiltration performance was investigated. The viscosity of the hemicellulose solution after extraction was considerably reduced with both prefiltration methods tested, leading to a substantial increase in flux during ultrafiltration. The highest flux achieved without pretreatment was about 75 l/m^2 h, and was increased to 225 and 440 l/m^2 h after dead-end filtration and microfiltration, respectively. However, the loss of hemicelluloses was considerable during microfiltration, but <5% during dead-end filtration. After prefiltration by dead-end filtration, hemicelluloses could be successfully concentrated and purified by ultrafiltration. Eighty percent of the initial volume was removed during concentration at an average flux of 155 l/m^2 h. At the same time, the concentration and purity of the hemicelluloses increased from 7.6 g/l and 15% to 31.6 g/l and 31%, respectively. The results obtained in this investigation indicate that dead-end filtration could be a useful form of pretreatment before ultrafiltration when recovering hemicelluloses extracted from wheat bran.

1. Introduction

Wheat is one of the most commonly cultivated cereal grains worldwide with an annual production of about 650 Mio tonnes [1]. The starch-rich endosperm of the whole grain is used in food production, but there is no profitable application for the bran that encloses the endosperm. However, this waste material could constitute a resource as it consists of more than 30% of the valuable hemicellulose arabinoxylan [2]. Arabinoxylan and other hemicelluloses have excellent properties for the production of oxygen barrier films for food packaging [3–7]. It has been shown that films produced from arabinoxylan have high mechanical strength and low oxygen permeability, and could therefore provide an alternative to fossil-based products in future packaging materials [4]. As a consequence of the increasing interest in arabinoxylan, various methods of extracting such molecules from wheat bran and other agricultural residues have been developed [8–13]. It has been found that arabinoxylan can be extracted at high yields without significant degradation of the polymeric structure [9].

The composition of the solution obtained after hemicellulose extraction depends on the raw material and the method used for extraction. In general, such solutions are complex mixtures of the product (arabinoxylan) and impurities consisting of co-extracted molecules and extraction chemicals. These impurities must be removed before the arabinoxylan can be used. However, such separation processes are often difficult because of the large number of substances present. Furthermore, the cost of separation can be high as solutions containing significant amounts of high-molecular-mass hemicelluloses have a high viscosity, increasing the energy required for pumping and stirring.

Membrane ultrafiltration is an attractive separation process for the recovery of hemicelluloses from mixtures obtained after extraction because of its energy efficiency and selectivity. The performance of ultrafiltration has been studied during the concentration and purification of galactoglucomannan from forestry streams [14–20] and large pilot-scale separation processes have been suggested [15,18,19]. Furthermore, ultrafiltration has been used to isolate arabinoxylan after extraction from agricultural residues [21–26]. However, more work is needed to develop a cost-efficient separation process with the aim to recover arabinoxylan after extraction from wheat bran.

In a recent investigation, we studied the performance of ultrafiltration of a solution containing arabinoxylan obtained from wheat bran under various operating conditions [27]. The maximal flux that could be achieved was below 70 l/m^2 h. This low flux was attributed to the high viscosity of the solution and the formation of a gel layer on the membrane surface. The objective of the

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present work was to investigate whether the flux during ultrafiltration could be increased by prefiltration of the arabinoxylan solution. Prefiltration could be an efficient means of removing gel-forming substances and decreasing the viscosity of the arabinoxylan solution. Two prefiltration methods were evaluated: microfiltration and dead-end filtration in a filter press. The influence on flux and retention during ultrafiltration was investigated under various operating conditions.

2. Materials and methods

2.1. Hemicellulose solution

Dry wheat bran was used as raw material to prepare the arabinoxylan solution used as feed in the membrane filtration and filtration experiments. First, the wheat bran was washed and treated with enzymes to degrade and remove the starch. Hemicelluloses were then extracted from the bran at high pH with a concentrated sodium hydroxide (NaOH) solution. At high pH, the ester bonds between hemicelluloses and other biomass components (mainly lignin and cellulose) are cleaved leading to the release of hemicelluloses from the biomass structure. Hemicelluloses with high molecular mass are most suitable for applications such as oxygen barrier films, and it is therefore desirable to maintain a high molecular mass of the hemicelluloses after extraction.

2.2. Equipment

2.2.1. Membranes

Tubular ceramic membranes from Atech Innovations GmbH (Gladbeck, Germany) were used for microfiltration and ultrafiltration. The material of the microfiltration and ultrafiltration membranes was α-alumina oxide and titanium dioxide, respectively. The microfiltration membrane had a pore size of 0.2 μm and the ultrafiltration membrane a nominal molecular weight cut-off of 10 kDa. Both membranes had 7 parallel feed flow channels, an outer diameter of 25.4 mm, and a total length of 1 m. The inner diameter of the feed flow channels was 6 mm, and the membrane area 0.132 m^2. The hydraulic resistance of the micro- and ultrafiltration membrane was calculated from the pure water flux to 2.9×10^{11} m^{-1} and 1.6×10^{12} m^{-1}, respectively.

2.2.2. Membrane filtration setup

Microfiltration and ultrafiltration experiments were performed in the same membrane filtration setup (Fig. 1). An M1 membrane module from Atech Innovations, in which either the ultrafiltration or the microfiltration membrane was inserted, was used. Two 200-l tanks and a centrifugal pump (NB32/25-20, ABS Pump Production, Mölndal, Sweden) were connected to the system. The first tank was used as a feed tank during the membrane filtration experiments. The second tank was mainly used during cleaning. The feed pressure and the cross-flow velocity in the feed flow channels of the membranes were regulated with a frequency converter (CDA3000, Lust Antriebstechnik GmbH, Lahnau, Germany) and a valve on the retentate side of the module. Pressure transmitters (dTrans p02, Jumo AB, Helsingborg, Sweden) were installed in the system to measure the pressure on the feed, P_F, and the retentate, P_R, and permeate sides, P_P, of the membrane. The transmembrane pressure (TMP) was calculated from the relation:

$$\mathrm{TMP} = \frac{P_F + P_R}{2} - P_P \qquad (1)$$

The TMP was controlled by manually adjusting a valve on the permeate side of the module. The feed flow was measured before the membrane module with a volume flow meter (Fischer&Porter Co. Ltd., Göttingen, Germany) and the permeate flow was measured with an electronic balance (PL6001-S, Metter-Toledo Inc., Columbus, OH). A Pt100 temperature probe was immersed in each of the feed tanks for temperature measurements. All data from the measuring devices were continuously recorded using LabView software (National Instruments Co., Austin, TX).

2.2.3. Filter press

Dead-end filtration was performed with a PF 0.1 H2 filter press (Larox Corp., Lappeenranta, Finland). The filter press included a 100-l feed tank equipped with an agitator, and an air-driven slurry pump (Wilden M2-P Champ, Wilden Pump & Engineering Co., Colton, CA). The filtration area was 0.1 m^2 and a 10 μm filter cloth (Hydrotech AB, Vellinge, Sweden) was used for filtration.

2.3. Experimental procedure

2.3.1. Membrane cleaning

Membranes were cleaned for 1 h before and after use with a 0.5 wt% solution of the alkaline cleaning agent Ultrasil 10 (Ecolab AB, Älvsjö, Sweden). The temperature, the TMP and the cross-flow velocity during cleaning were 50 °C, 1.0 bar and 3 m/s, respectively. After cleaning, the membrane was rinsed thoroughly with deionized water in order to remove the cleaning agent from the system.

2.3.2. Prefiltration by microfiltration

The hemicellulose solution obtained from the alkali extraction process was prefiltered by microfiltration using the setup shown in Fig. 1. The initial volume of the solution in the feed tank was about 195 l. Microfiltration was carried out at a temperature of 80 °C, a TMP of 1.0 bar, and a cross-flow velocity of 4 m/s in the feed flow channels of the membrane. The retentate stream was recirculated to the feed tank, while the permeate stream was withdrawn from the system and collected. Microfiltration was stopped when a permeate volume of 60 l had been obtained, which corresponds to a volume reduction of about 30%.

2.3.3. Prefiltration by dead-end filtration

As an alternative to microfiltration, dead-end filtration was used for prefiltration. Calcinated and purified kieselguhr (AppliChem GmbH, Darmstadt, Germany) was added to the hemicellulose solution and the mixture was mixed for 30 min prior to filtration. The concentration of kieselguhr in the mixture was 2 wt%. The temperature and the pressure during filtration were 50 °C and 4 bar, respectively. Several filtration cycles were performed in order to collect a sufficient amount of filtrate for the

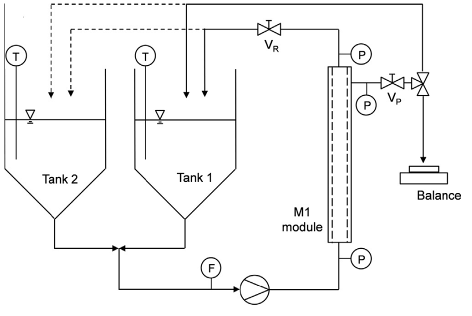

Fig. 1. Schematic of the experimental setup for microfiltration and ultrafiltration. V_R: Retentate valve; V_P: Permeate valve; P: Pressure transmitter; T: Temperature probe; F: Flow meter.

ultrafiltration experiments. In each cycle, about 75 l of feed solution was fed into the feed tank and about 60 l of filtrate was recovered before dead-end filtration was discontinued.

2.3.4. Study of ultrafiltration performance

The influence of the operating conditions (TMP, cross-flow velocity) on flux and retention during ultrafiltration was investigated. The study was performed with three different feed solutions: the hemicellulose solution obtained from the extraction process, and the filtrates obtained after microfiltration and dead-end filtration. Between the experiments with different feed solutions, the membrane was cleaned according to the method described above.

In all three cases the same experimental procedure was used. First, a 0.1 M NaOH solution was fed into tank 1 of the experimental setup (Fig. 1) and circulated through the system at a temperature of 60 °C. About 60 l of feed solution was fed into tank 2 and heated to the same temperature as the NaOH solution in tank 1. The feed was switched from tank 1 to tank 2, and the NaOH solution was displaced from the system. The solution was then further heated to 80 °C and the cross-flow velocity was adjusted, then the permeate valve was opened in order to adjust the TMP. Both the permeate and the retentate stream were returned to tank 2 during the study. Ultrafiltration of the three different feed solutions was carried out at a constant temperature (80 °C) and at the cross-flow velocities and TMPs given in Table 1. Each experimental series was begun at the highest cross-flow velocity and lowest TMP in order to minimize the formation of a cake layer on the membrane surface. The flux was recorded at each combination of cross-flow velocity and TMP for about 30 min before samples were taken from the permeate and the feed tank. In order to avoid fouling the ultrafiltration membrane unnecessarily, the TMP was not further increased when a marked leveling-off of the flux was observed.

Permeate was withdrawn from the ultrafiltration system in an experiment designed to concentrate the hemicelluloses in a solution prefiltered by dead-end filtration. The initial volume in the feed tank was 130 l and concentration was carried out until a volume reduction of 80% had been achieved. The cross-flow velocity, the TMP, and the temperature of the feed were constant throughout the experiment, at 5 m/s, 1.2 bar and 80 °C, respectively. Samples were taken from the permeate and the feed tank at regular intervals.

2.4. Analytical methods

2.4.1. Total solids and sodium hydroxide

Samples were dried for 24 h in an oven at a temperature of 105 °C. The total solids content was then determined from the dry weight of the residue. The dry sample was further heated to 575 °C, and this temperature maintained for 3 h. After cooling to room temperature the ash content was determined gravimetrically. The content of NaOH was calculated from the ash content by multiplying by a correction factor of 1.29. Further details concerning the correction factor can be found in our previous publication [27].

Table 1
Operating conditions used in the studies of the three feed solutions.

Feed solution	Cross-flow velocity (m/s)	TMP (bar)
Hemicellulose solution from extraction process	3	0.4; 0.6; 0.8; 1.0
	4	0.4; 0.6; 0.8; 1.0;1.2; 1.4; 1.6
	5	0.4; 0.6; 0.8; 1.0;1.2; 1.4; 1.6
Solution prefiltered by microfiltration	3	0.6, 0.8, 1.0, 1.2, 1.4
	4	0.6, 0.8, 1.0, 1.2, 1.4, 1.6
Solution prefiltered by dead-end filtration	3	0.6, 0.8, 1.0, 1.2, 1.4, 1.6
	4	0.6; 0.8; 1.0;1.2; 1.4; 1.6
	5	0.6; 0.8; 1.0;1.2; 1.4, 1.6

2.4.2. Hemicelluloses

The concentration of hemicelluloses was determined by first degrading the hemicellulose molecules to monomeric sugars using a standardized method for acid hydrolysis [28]. The concentration of the monomeric sugars D-galactose, D-glucose, D-xylose, D-mannose, and L-arabinose was then measured using high-performance anion-exchange chromatography coupled with pulsed amperometric detection. The chromatography system (ICS-3000, Dionex Corp., Sunnyvale, CA) was equipped with a Carbo Pac PA1 analytical column (Dionex Corp.). Deionized water was used as eluent at a flow rate of 1 ml/min, and the column was cleaned with a solution of 200 mM NaOH dissolved in 170 mM sodium acetate. The sample injection volume was 10 µl. The concentration of hemicelluloses was defined as the sum of the monomeric sugars after anhydro corrections of 0.88 and 0.90 for pentoses and hexoses, respectively.

The molecular mass distribution of hemicelluloses was determined by size exclusion chromatography using a Waters 600E chromatography system (Waters, Milford, MA) equipped with a refractive index detector (model 410, Waters). The analytical column was packed with 30 cm Superdex 30 and 30 cm Superdex 200 (GE Healthcare, Uppsala, Sweden). A 125 mM NaOH solution was used as eluent at a flow rate of 1 ml/min. The system was calibrated with polyethylene glycol standards with peak molecular masses of 0.4, 4, 10 and 35 kg/mol (Merck Schuchardt OHG, Hohenbrunn, Germany).

2.4.3. Acid-insoluble solids and acid-soluble lignin

In order to determine the content of acid-insoluble solids and acid-soluble lignin the sample was first subjected to acid hydrolysis (standardized method [28]). Acid-insoluble solids were then removed with a filter crucible with a maximal pore size of 16 µm (Schott AG, Mainz, Germany), and quantified gravimetrically after drying for 24 h at 105 °C. The content of acid-soluble lignin was determined by measuring the UV absorbance of the filtrate at a wavelength of 320 nm in a spectrophotometer (UV-160, Shimadzu Corp., Kyoto, Japan). An extinction coefficient of 30 l/g cm, was used [29].

2.4.4. Viscosity and turbidity

Viscosity measurements were performed in a Kinexus Pro rotational rheometer (Malvern Instruments Ltd., Worcestershire, UK) using a cup-and-bob geometry. The torque range of the rheometer was 0.05 µN m to 200 mN m. The system allowed the temperature of the sample to be kept constant during the measurements. The apparent viscosity was measured at a temperature of 80 °C in the shear rate range 1–100 s^{-1}.

The turbidity was measured in a turbidimeter (2100P ISO, HACH Co., Loveland, CO). The instrument was calibrated with stabilized formazin standards (HACH) of 0, 20, 100, and 800 nephelometric turbidity units (NTU).

3. Results and discussion

3.1. Composition of the hemicellulose solution

The concentration of hemicelluloses in the solution obtained from the extraction process was about 7.9 g/l. Of the hemicellulose

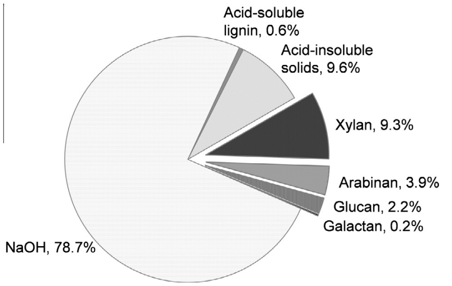

Fig. 2. Composition of total solids in the hemicellulose solution after extraction (in wt%). The concentration of mannan in the solution was zero and is therefore not included in the figure. The total solids content was 50.8 ± 1.9 g/l.

molecules present, about 85 wt% was arabinoxylan, which is the predominant hemicellulose in wheat bran. The average molecular mass of hemicelluloses after extraction was about 90 kDa, indicating that the molecules were not significantly degraded during the extraction process.

Hemicelluloses were defined as the sum of xylan, arabinan, glucan, galactan, and mannan and constituted about 16 wt% of the total solids (about 50.8 g/l) in the solution (see Fig. 2). The residual solids are undesired impurities that must be removed from the final product. Sodium hydroxide, used to solubilize the hemicelluloses in wheat bran during extraction, was the main impurity present in the solution. The concentration of sodium hydroxide was about 40 g/l, giving rise to a high solution pH of about 13.3. Other impurities in the solution were particles and other acid-insoluble substances that were derived from the wheat bran. The turbidity of the solution due to the presence of particles was about 690 NTU, and the total concentration of acid-insoluble solids was about 4.9 g/l. It was assumed that lignin, proteins, pectins, and fats contribute to the fraction of acid-insoluble solids. The viscosity of the solution was about 4.8 mPa s, measured at a temperature of 80 °C and a shear rate of 100 s^{-1}. Thus, the solution was about 14 times more viscous than water.

3.2. Ultrafiltration of the hemicellulose solution after extraction

The separation of hemicelluloses from impurities was first studied with the hemicellulose solution obtained from the extraction process. A relatively low flux (<75 l/m^2 h) was observed in these experiments, as show in Fig. 3. As expected, the flux increased with TMP for all three cross-flow velocities. However, even at the highest cross-flow velocity of 5 m/s, the flux increase was only small when the TMP exceeded 0.8 bar. This observation can be explained by the formation of a gel layer on the membrane surface already at a pressure below 1 bar. The formation of gel layers is a well-known phenomenon that can cause flux limitation during ultrafiltration. The presence of gel layers during membrane filtration of solutions containing hemicelluloses has been reported previously, e.g., by Persson et al. [17], Hasan et al. [30], and Schlesinger et al. [31].

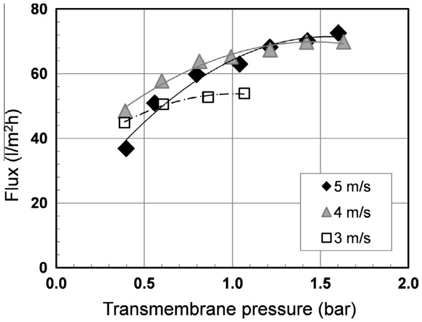

Fig. 3. Flux as a function of transmembrane pressure and cross-flow velocity during ultrafiltration of the hemicellulose solution obtained from the extraction process.

A higher maximal flux was achieved during ultrafiltration by increasing the cross-flow velocity, and thus the shear at the membrane surface. It can be assumed that the higher shear reduces the thickness of the gel layer and thus its resistance. However, this effect was not significant when increasing the cross-flow velocity from 4 to 5 m/s; the maximal fluxes achieved at these cross-flow velocities were very similar, i.e. 70 and 73 l/m^2 h.

High hemicellulose retention, about 96%, was observed during ultrafiltration of the solution after extraction for all the operating conditions. The retention of the undesirable acid-insoluble solids was ~90%, whereas the major impurity, sodium hydroxide, was found to pass through the ultrafiltration membrane almost freely (retention of 3%). Thus, while hemicelluloses can be separated from NaOH, only a small fraction of the acid-insoluble solids can be removed from hemicelluloses by ultrafiltration. It can thus be concluded that, apart from the relatively low flux (Fig. 3), acid-insoluble solids in the final product could be a problem. Such impurities would decrease the quality of oxygen barrier films produced from hemicelluloses after separation.

3.3. Improvement of the flux by prefiltration

Several researchers have shown that appropriate pretreatment prior to membrane filtration can increase the flux by removing impurities from a solution or by modifying them [16,32,33]. In the present work, the hemicellulose solution obtained after extraction was pretreated by two filtration methods and the influence on ultrafiltration performance was investigated.

Figs. 4 and 5 show the flux during ultrafiltration of the hemicellulose solution after dead-end filtration and microfiltration under various operating conditions. It can be seen that both prefiltration methods increased the flux considerably. For example, at a cross-flow velocity of 4 m/s and a TMP of 1.6 bar the flux without prefiltration was 70 l/m^2 h (Fig. 3), but increased to 225 and 440 l/m^2 h after dead-end filtration and microfiltration, respectively. Koivula et al. [32] observed similar flux improvement when pretreating hemicelluloses-containing wood hydrolysate before ultrafiltration using a pulsed corona discharge method. They reported a sixfold increase in flux in their investigation.

The flux during ultrafiltration of a solution containing hemicelluloses extracted from wheat bran is significantly influenced by the viscosity of the feed solution, as shown in our previous study [27]. Differences in the viscosity between the hemicellulose solution after extraction and the solutions after prefiltration could therefore explain the substantial increase in flux resulting from prefiltration. Fig. 6 shows the apparent viscosity as a function of the shear rate for the hemicellulose solution and the two solutions after prefiltration. It can be seen that the apparent viscosity was reduced markedly by both prefiltration methods. At the highest shear rate, the viscosity was 4.8 mPa s in the solution after extraction, but only 1.8 mPa s after dead-end filtration and 1.1 mPa s after microfiltration. Furthermore, the rheological behavior of the three solutions differed considerably. While the solution obtained from the extraction process was sheer-thinning, i.e. the apparent viscosity decreased with increasing shear rate, the apparent viscosity of the

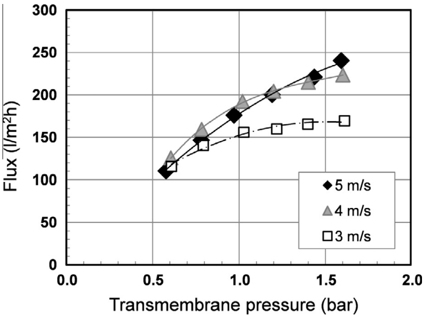

Fig. 4. Ultrafiltration of the hemicellulose solution after dead-end filtration. Influence of transmembrane pressure and cross-flow velocity on flux.

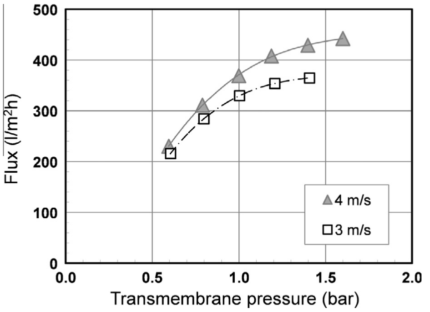

Fig. 5. Ultrafiltration of the hemicellulose solution after microfiltration. Influence of transmembrane pressure and cross-flow velocity on flux.

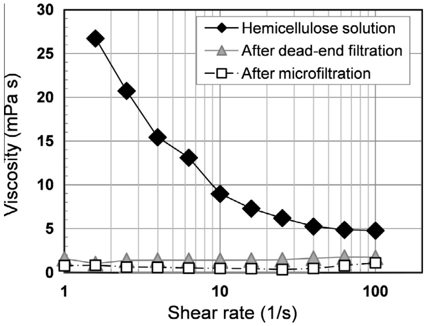

Fig. 6. Apparent viscosity of the hemicellulose solution after extraction, dead-end filtration and microfiltration. Measurements were performed at a temperature of 80 °C.

solution after dead-end filtration and microfiltration was independent of the shear rate (Newtonian behavior). These results showed that both prefiltration techniques remove some of the substances responsible for the high viscosity in the hemicellulose solution after extraction.

3.4. Influence of prefiltration on the composition of the hemicellulose solution

The flux during ultrafiltration could be increased by more than a factor 3 by dead-end filtration and a factor 6 by microfiltration of the hemicellulose solution (see Section 3.3). However, apart from increasing the flux, it is important that the loss of hemicelluloses is not significant in the prefiltration step. The influence of dead-end filtration and microfiltration on the composition of the hemicellulose solution was therefore investigated.

The two prefiltration techniques altered the concentration of the main components in the solution to various degrees, as can be seen in Table 2. After dead-end filtration the concentration of hemicelluloses was almost unchanged. The impurities NaOH and acid-soluble lignin were not removed, but the concentration of acid-insoluble solids was decreased significantly, from 4.9 g/l in the hemicellulose solution to 2.2 g/l in the filtrate after dead-end filtration. Microfiltration was even more efficient in the removal of acid-insoluble solids. However, this technique also reduced the concentration of hemicelluloses. As can be seen in Table 2, only about 4% of the hemicelluloses was recovered in the permeate, thus using microfiltration for prefiltration will result in a considerable loss of product.

The high retention of hemicelluloses during microfiltration was unexpected as hemicellulose molecules are significantly smaller than the pore size of the microfiltration membrane. In addition, the initial flux during microfiltration (data not shown) was found to be of the same magnitude as the flux during ultrafiltration of the hemicellulose solution after extraction, and thus surprisingly low. These observations indicate that the membrane pore size is of minor importance for its performance during membrane filtration of the hemicellulose solution after extraction. Instead, flux and retention are largely determined by the gel layer formed on the membrane surface. Previous investigations confirm that secondary layers formed on the surface of a microfiltration membrane can lead to high retention of small macromolecules [30,34].

Fig. 7 presents the size distribution of hemicelluloses dissolved in the solution after extraction, and in the solutions after prefiltration. As expected, the size of the hemicelluloses molecules was similar in the hemicellulose solution and the solution after dead-end filtration. However, in the solution after microfiltration the fraction of hemicelluloses with high molecular mass (>10 kDa) was significantly smaller, indicating that especially high-molecular mass hemicelluloses were lost during prefiltration by microfiltration.

3.5. Ultrafiltration performance during concentration of hemicelluloses after prefiltration

In an industrial separation process for isolating hemicelluloses from a mixture after extraction, the impurities should be removed

Table 2
Concentration of various components in the hemicellulose solution after extraction, and in the filtrate after dead-end filtration, and the permeate after microfiltration.

Total composition	Hemicellulose solution	Filtrate after dead-end filtration	Permeate after microfiltration
Total solids (g/l)	50.8 ± 1.9	49.5 ± 0.7	41.9 ± 0.9
NaOH (g/l)	40.0 ± 1.9	41.8 ± 0.4	40.7 ± 0.6
Hemicelluloses (g/l)	7.9 ± 0.3	7.8 ± 0.3	0.3 ± 0.1
Acid-insoluble solids (g/l)	4.9 ± 0.5	2.2 ± 0.3	0.5 ± 0.0
Acid-soluble lignin (g/l)	0.3 ± 0.0	0.3 ± 0.1	0.3 ± 0.1

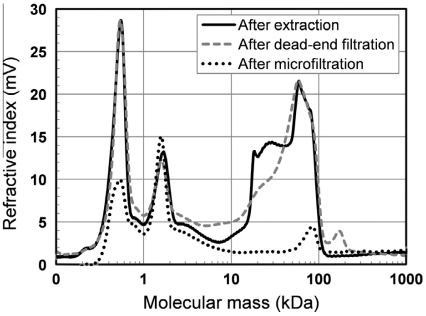

Fig. 7. Size distribution of the hemicelluloses in the solution after extraction, after dead-end filtration, and after microfiltration.

with the ultrafiltration permeate, and the hemicelluloses be concentrated in the retentate. If such a concentration process is carried out directly after extraction, low initial flux and considerable flux decline with increasing hemicellulose concentration can be expected [27]. Achieving high concentration and purity of hemicelluloses will thus require a large membrane area during ultrafiltration, decreasing the cost-efficiency of the process. For this reason, the flux during the concentration of hemicelluloses was studied for a solution that had been prefiltered prior to ultrafiltration. A further aim of this concentration study was to investigate the extent to which the concentration and purity of hemicelluloses could be increased by ultrafiltration. The prefiltration method chosen for this concentration process was dead-end filtration due to its positive effect on ultrafiltration flux and the low product loss.

As shown in Fig. 8, high flux was observed during concentration of the hemicellulose solution after prefiltration. The hemicelluloses in the solution could be concentrated up to a volume reduction of 80%, at which time the experiment had to be stopped due to the small volume remaining in the system. The average flux in the concentration experiment was 155 l/m^2 h, i.e. about twice the flux achieved during ultrafiltration of the hemicellulose solution after extraction (see Fig. 3). The viscosity of the solution increased steeply at the end of the concentration process, explaining the more significant flux decline at higher volume reduction.

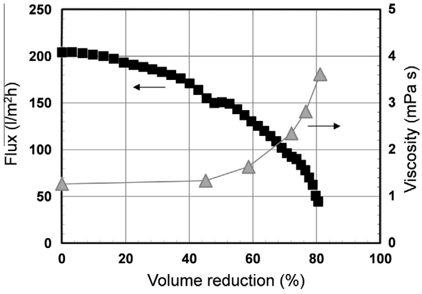

Fig. 8. Ultrafiltration flux and viscosity during concentration of hemicelluloses in a solution prefiltered by dead-end filtration. Temperature 80 °C, cross-flow velocity 5 m/s and transmembrane pressure 1.2 bar.

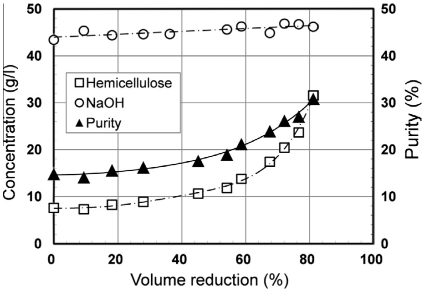

Fig. 9. Concentration of hemicelluloses and NaOH, and purity of the hemicellulose solution during the concentration process.

The initial concentration and purity of hemicelluloses in the solution was about 7.6 g/l and 15%. Due to the high retention of hemicelluloses (~90%) and the low retention of NaOH (~3%) hemicelluloses were concentrated and purified with increasing volume reduction. At the end of the experiment the hemicellulose concentration increased to 31.6 g/l. At the same time, the concentration of the main impurity, NaOH, remained almost constant (see Fig. 9). As a consequence, the purity of hemicelluloses in the solution increased from 15 to 31%. In Fig. 9 it can be seen that the most significant increase in hemicellulose concentration occurred towards the end of concentration. Thus, achieving a volume reduction greater than 80% could be beneficial, as this would provide a more concentrated hemicellulose stream with higher purity. The use of diafiltration subsequent to the concentration process could further increase the product purity by enhancing the removal of NaOH.

4. Conclusions

Hemicelluloses extracted from wheat bran can be concentrated and purified by ultrafiltration. The objective of this work was to investigate whether the performance of ultrafiltration could be improved by prefiltering the hemicellulose solution. Using microfiltration prior to ultrafiltration was found to have a detrimental effect on product yield, and is therefore not recommended. However, the use of dead-end filtration improved ultrafiltration performance considerably. The flux was increased more than threefold. A smaller ultrafiltration plant would thus be required if the solution were to be prefiltered after extraction, resulting in a lower investment cost. Furthermore, dead-end filtration enhanced the removal of undesirable acid-insoluble solids. Thus, as well as increasing flux, the product purity was increased. After dead-end filtration it was possible to concentrate hemicelluloses from 7.6 to 31.6 g/l at a high average flux of 155 l/m^2 h. While the retention of hemicelluloses was high (~90%), the main impurity (NaOH) could pass through the membrane almost freely. The results of this investigation indicate that an additional prefiltration step after hemicellulose extraction, consisting of dead-end filtration, can improve cost-efficiency and product quality during the recovery of hemicelluloses from wheat bran.

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References

[1] FAO, Food and agriculture organization of the united nations. <http://faostat.fao. org>, 2012.

[2] A. Ebringerová, T. Heinze, Xylan and xylan derivatives – biopolymers with valuable properties 1, Macromol. Rapid Commun. 21 (2000) 542–556.

[3] M. Gröndahl, L. Eriksson, P. Gatenholm, Material properties of plasticized hardwood xylans for potential application as oxygen barrier films, Biomacromolecules 5 (2004) 1528–1535.

[4] N.M.L. Hansen, D. Plackett, Sustainable films and coatings from hemicelluloses: a review, Biomacromolecules 9 (2008) 1493–1505.

[5] J. Hartman, A.-C. Albertsson, M. Söderqvist Lindblad, J. Sjöberg, Oxygen barrier materials from renewable sources: material properties of softwood hemicellulose-based films, J. Appl. Polym. Sci. 100 (2006) 2985–2991.

[6] J. Hartman, A.-C. Albertsson, J. Sjöberg, Surface- and bulk-modified galactoglucomannan hemicellulose films and film laminates fro versatile oxygen barriers, Biomacromolecules 7 (2006) 1983–1989.

[7] A.I. Yaich, U. Edlund, A.-C. Albertsson, Wood hydrolysate barriers: performance controlled via selective recovery, Biomacromolecules 13 (2012) 466–473.

[8] R.C. Sun, J. Tomkinson, Characterization of hemicelluloses obtained by classical and ultrasonically assisted extraction from wheat straw, Carbohydr. Polym. 50 (2002) 263–271.

[9] M.E.F. Bergmans, G. Beldman, H. Gruppen, A.G.J. Voragen, Optimisation of the selective extraction of (glucurono)arabinoxylans from wheat bran: use of barium and calcium hydroxide solution at elevated temperatures, J. Cereal. Sci. 23 (1996) 235–245.

[10] A. Höije, M. Gröndahl, K. Tømmeraas, P. Gatenholm, Isolation and characterization of physicochemical and material properties of arabinoxylans from barley husks, Carbohydr. Polym. 61 (2005) 266–275.

[11] A.A. Roos, T. Persson, H. Krawczyk, G. Zacchi, H. Stålbrand, Extraction of water-soluble hemicelluloses from barley husks, Bioresour. Technol. 100 (2009) 763–769.

[12] W.G. Glasser, W.E. Kaar, R.K. Jain, J.E. Sealey, Isolation options for non-celllulosic heteropolysaccharides (HetPS), Cellulose 7 (2000) 299–317.

[13] J.M. Fang, R.C. Sun, D. Salisbury, P. Fowler, J. Tomkinson, Comparative study of hemicelluloses from wheat straw by alkali and hydrogen peroxide extractions, Polym. Degrad. Stabil. 66 (1999) 423–432.

[14] M. Al Manasrah, M. Kallioinen, H. Ilvesniemi, M. Mänttäri, Recovery of galactoglucomannan from wood hydrolysate using regenerated cellulose ultrafiltration membranes, Bioresour. Technol. 114 (2012) 375–381.

[15] T. Persson, A.-K. Nordin, G. Zacchi, A.-S. Jönsson, Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce, Appl. Biochem. Biotechnol. 137 (2007) 741–752.

[16] T. Persson, A.-S. Jönsson, Fouling of ultrafiltration membranes during isolation of hemicelluloses in the forest industry, Schol. Res. Exch. Eng. (2009). doi:10.3814/2009/624012.

[17] T. Persson, A.-S. Jönsson, Isolation of hemicelluloses by ultrafiltration of thermomechanical pulp mill process water – Influence of operating conditions, Chem. Eng. Res. Des. 88 (2010) 1548–1554.

[18] T. Persson, H. Krawczyk, A.-K. Nordin, A.-S. Jönsson, Fractionation of process water in thermomechanical pulp mills, Bioresour. Technol. 101 (2010) 3884–3892.

[19] A. Sundberg, S. Willför, P. Rehn, B. Holmbom, Can water-soluble O-acetyl-galactoglucomannans be isolated in large-scale from TMP, in: Proc. 12th Int. Symposium on Wood and Pulping Chemistry, University of Wisconsin-Madison, vol. 2, 2003.

[20] S. Willför, P. Rehn, A. Sundberg, K. Sundberg, B. Holmbom, Recovery of water-soluble acetylgalactoglucomannans from mechanical pulp of spruce, Tappi J. 2 (2003) 27–32.

[21] K. Swennen, C.M. Courtin, B. van der Bruggen, C. Vandecasteele, J.A. Delcour, Ultrafiltration and ethanol precipitation for isolation of arabinoxylooligosaccharides with different structures, Carbohydr. Polym. 62 (2005) 283–292.

[22] H. Krawczyk, T. Persson, A. Andersson, A.-S. Jönsson, Isolation of hemicelluloses from barley husks, Food Bioprod. Process. 86 (2008) 31–36.

[23] J. Hollmann, M.G. Lindhauer, Pilot-scale isolation of glucuronoarabinoxylans from wheat bran, Carbohydr. Polym. 59 (2005) 225–230.

[24] R. Zeitoun, P.Y. Pontalier, P. Marechal, L. Rigal, Twin-screw extrusion for hemicellulose recovery: Influence on extract purity and purification performance, Bioresour. Technol. 101 (2010) 9348–9354.

[25] L. Jacquemin, R. Zeitoun, C. Sablayrolles, P.-Y. Pontalier, L. Rigal, Evaluation of the technical and environmental performances of extraction and purification processes of arabinoxylans from wheat straw and bran, Proc. Biochem. 47 (2012) 373–380.

[26] J. Jorda, P. Marechal, L. Rigal, P.Y. Pontalier, Biopolymer purification by ultrafiltration, Desalination 148 (2002) 187–191.

[27] H. Krawczyk, A. Arkell, A.-S. Jönsson, Membrane performance during ultrafiltration of a high-viscosity solution containing hemicelluloses from wheat bran, Sep. Purif. Technol. 83 (2011) 144–150.

[28] R. Ruiz, T. Ehrman, Laboratory Analytical Procedure LAP-014: Dilute Acid Hydrolysis Procedure for Determination of Total Sugars in The Liquid Fraction of Process Samples, NREL, Midwest Research Institute for the Department of Energy, USA, 1996.

[29] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Laboratory Analytical Procedure (LAP): Determination of Structural Carbohydrates and Lignin in Biomass, NREL, Midwest Research Institute for the Department of Energy, USA, 2008.

[30] A. Hasan, R. Yasarla, B.V. Ramarao, T.E. Amidon, Separation of lignocellulosic hydrolyzate components using ceramic microfilters, J. Wood Chem. Technol. 31 (2011) 357–383.

[31] R. Schlesinger, T. Röder, G. Götzinger, H. Sixta, M. Harasek, A. Friedl, Influence of hemicellulose aggregate and gel layer formation on flux and retention during nanofiltration of alkaline solutions, Desalination 175 (2005) 121–134.

[32] E. Koivula, M. Kallioinen, S. Preis, L. Testova, H. Sixta, M. Mänttäri, Evaluation of various pretreatment methods to manage fouling in ultrafiltration of wood hydrolysates, Sep. Purif. Technol. 83 (2011) 50–56.

[33] H.E. Cutler, S.M. Husson, S.R. Wickramasinghe, Prefiltration to suppress protein fouling of microfiltration membranes, Sep. Purif. Technol. 89 (2012) 329–336.

[34] H. Krawczyk, A.-S. Jönsson, Separation of dispersed substances and galactoglucomannan in thermomechanical pulp process water by microfiltration, Sep. Purif. Techol. 79 (2011) 43–49.

Paper VI

Evaluation of membrane performance and cost estimates during recovery of sodium hydroxide in a hemicellulose extraction process by nanofiltration

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Abstract

The recovery of the alkaline solvent from a residual stream after the extraction of hemicelluloses in wheat bran was investigated. The solution was withdrawn from an ultrafiltration (UF) process in which hemicelluloses were recovered. The UF permeate, containing mainly NaOH, lignin and mono- and oligosaccharides, was treated by nanofiltration (NF). Seven NF membranes were tested in a parametric study, and the two membranes showing the best performance were further evaluated in a concentration study. The mean flux of a Koch SelRO MPF 36 and a Microdyn-Nadir NP010 membrane was about 200 l/m^2 h during concentration to a volume reduction of 0.75. The retention of NaOH was <20%, while the retention of lignin and sugars was about 70% and >95%, respectively. Cost estimates for a NaOH recovery process indicated that an NF plant would have a pay-back time of less than two months if the plant was run continuously, and seven months if it was used 25% of the time.

Key words: alkaline solvent recovery; nanofiltration; lignin; hemicelluloses; biorefinery

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1. Introduction

Hemicelluloses in wheat bran and barley husks can be recovered by alkaline extraction using sodium hydroxide (NaOH) [1-4]. The dissolved hemicelluloses can then be concentrated and purified by ultrafiltration (UF) [5,6], and used for the production of oxygen barrier films for food packaging [7,8]. The UF permeate is regarded as waste water. However, if it would be possible to remove lignin and low-molecular mass sugars, NaOH in the UF permeate could be reused in the alkaline extraction process. One feasible way of doing this is by nanofiltration (NF).

Although NF is an established technique for the regeneration of alkaline clean-in-place solutions in the food industry [9,10] only a limited number of investigations on using NF for the recovery of alkaline solvents in biorefinery processes have been published [11,12].

The objective of this study was to investigate the removal of organic impurities (lignin and sugars) from an alkaline hemicellulose extraction solution by NF to obtain an NF permeate pure enough to be reused for alkaline extraction of agricultural residues, and thus reduce the cost of NaOH. The performance of seven NF membranes with cut-offs in the interval 200-1400 Da was first evaluated in a parametric study. The two membranes showing the best performance were further investigated in a concentration study. Cost estimates of the NF process were made based on experimental data from this study, together with data from membrane manufacturers, and our own experience of similar installations.

2. Materials and methods

2.1. Process solution

The process solution used in the experiments of this work was withdrawn from a hemicellulose isolation process. In this process hemicelluloses are first extracted from wheat bran using NaOH. The alkaline extract is subsequently prefiltered in a filter press and hemicelluloses then concentrated by ultrafiltration using a 10 kDa ceramic membrane. The UF permeate is a waste water, containing a substantial amount of NaOH that could be reused for extraction. UF permeate was used as feed in the NF experiments. Its composition is given in Table 1.

Table 1

Characteristics of the process solution used in the experiments. UV absorbance at 280 nm is a measure of lignin content. Concentrations are average values from eight experiments.

	Process solution
Total solids (g/l)	43.4
NaOH (g/l)	41.0
UV absorbance	33.7
Sugars (g/l)	0.69
Arabinan (g/l)	0.11
Galactan (g/l)	0.04
Glucan (g/l)	0.21
Xylan (g/l)	0.33

2.2. Membranes

The performance of seven alkali resistant NF membranes was investigated in a parametric study. The characteristics of the membranes are given in Table 2. Four flat-sheet polymeric and two hollow-fibre polymeric NF membranes with nominal cut-offs from 200 to 1400 Da were used. The inner diameter of the hollow-fibre membranes from Pentair Inc. was 0.8 mm, and the modules contained 100 hollow-fibres, 1 m long. The ceramic membrane from Tami Industries was 1.2 m long and had eight parallel flow channels with an inner diameter of 6 mm.

Table 2

Characteristics of the seven nanofiltration membranes tested in the parametric study.

Manufacturer & Membrane	Type	MWCO (Da)	Retention NaCl (%)	Max. press (bar)	Max. temp. (°C)
Koch Membrane Systems Inc., USA					
SelRO MPF 34	Flat, polymeric	200	35	35	70 (max 15 bar)
SelRO MPF 36	Flat, polymeric	1000	10	35	60 (max 25 bar)
Microdyn-Nadir GmbH, Germany					
NP010	Flat, polymeric	1000-1400	10	40	95
NP030	Flat, polymeric	500-700	30	40	95
Pentair Inc., USA					
HFR 2[1]	Hollow-fibre, polymeric	< 1000	n.a.	5	40
HFC 3	Hollow-fibre, polymeric	1000	n.a.	5	40
Tami Industries, France					
Tami Inside	Ceramic	1000	n.a.	10	350

MWCO = molecular weight cut-off

[1] Membrane still under development, retention data not available (n.a.).

2.3. Equipment

Two experimental setups were used in the investigation; one in the experiments with polymeric membranes, and the other in the experiment with the ceramic membrane. The main components of the laboratory equipment used in the polymeric membrane experiments were an isolated and heat controlled tank, a displacement pump (Hydra-cell D25XL, Wanner, Minneapolis, MN, USA) and either four flat-sheet membrane modules connected in parallel, (shown in Fig. 1), a hollow-fibre module or a DDS 20 plate-and-frame module (Alfa Laval A/S, Nakskov, Denmark). A Pt-100 temperature sensor (Pentronic, Gunnebo, Sweden) was immersed in the feed tank and connected to a temperature regulator (Shinko MCM, Shinko Europe BV, Haarsteeg, the Netherlands) controlling the temperature in the feed tank by an electrical heater. The pump was connected to a frequency converter (ELEX 4000, Bergkvist & Co AB, Gothenburg, Sweden) controlling the flow rate. The permeate flow was measured with an electronic balance (PL6001-S, Mettler-Toledo Inc., Columbus, OH, USA).

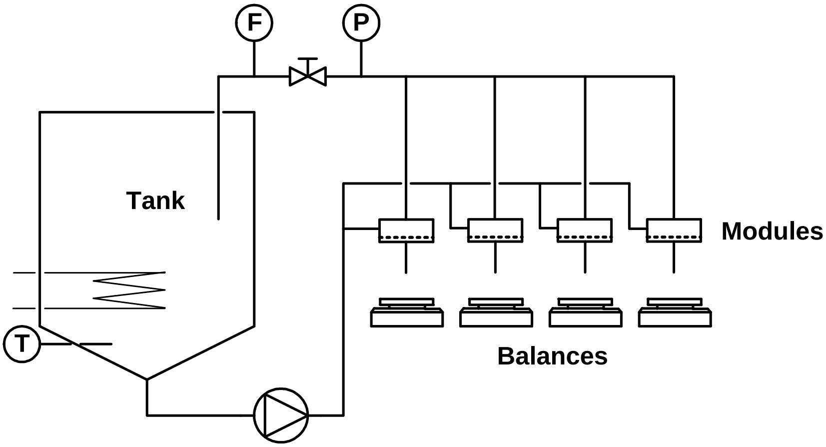


Fig. 1. Flow sheet of the equipment used in the flat-sheet membrane experiments.
F = flow meter, P = pressure transmitter and T = temperature sensor.

The setup with four modules connected in parallel was used in the parametric studies with the flat-sheet membranes. Each module was equipped with a circular flat membrane with an area of 0.00196 m^2. Duplicates of each membrane were studied simultaneously, i.e., two samples from one membrane in two modules and two samples from another membrane in the other two modules. During the concentration studies, the same flat-sheet membrane was used in all four modules.

In the experiments with hollow-fibre membranes, the flat-sheet membrane modules were replaced with a single hollow-fibre module. The membrane area of each hollow-fibre membrane element was 0.23 m^2. A concentration study with one membrane was carried out in the DDS 20 module. This module was equipped with four double-sided membrane discs with a total membrane area of 0.144 m^2.

The second setup was used in the parametric study with the ceramic membrane. In this experiment the same equipment was used as in the UF experiment, described in a previous article [6]. The membrane area of the ceramic membrane was 0.20 m^2.

2.4. Experimental procedure

All membranes were cleaned for 1 h before and after each experiment, using a 0.5 wt% solution of the alkaline cleaning agent Ultrasil 10 (Ecolab AB, Älvsjö, Sweden) for the polymeric membranes, and Ultrasil 11 (Ecolab) for the ceramic membrane. After cleaning, the membranes were rinsed thoroughly with deionized water in order to wash out the cleaning agent from the system, and the pure water flux was measured at 30°C.

During the parametric studies, both the retentate and the permeate were recycled to the feed tank in order to keep the concentration constant. The temperature during the experiments with the membranes from Tami and Microdyn-Nadir was 80°C, which is the operating temperature during the UF stage in the hemicellulose extraction process. Experiments were performed at maximum temperature of the other polymeric membranes, which means that the temperature was 40°C and 60°C in the experiments with membranes from Pentair and Koch. Cross-flow velocities recommended by the manufacturers were used. The cross-flow velocities were 0.45 and 0.90 m/s during experiments with the polymeric membranes and 3, 4 and 5 m/s in the experiment with the ceramic membrane. The transmembrane pressure (TMP) was first increased stepwise at the highest cross-flow velocity in order to reduce the influence of a possible cake layer on the membrane. The TMP was then decreased to the initial value, and the cross-flow velocity reduced. TMP was increased once again at the lower velocity. The flux was recorded at each combination of cross-flow velocity and TMP for about 15 min before samples were withdrawn from the permeate and the feed tank.

The Koch SelRO MPF 36 and Microdyn-Nadir NP010 membranes were found to be the most suitable in the parametric studies, and were thus used in a concentration study. During the concentration study, the same flat-sheet membrane was used in all four modules (Fig. 1). Both retentate and permeate were initially recycled to the feed tank, while the TMP was gradually increased to the final operating pressure of 15 bar. The concentration was then increased by withdrawal of permeate while recirculating the retentate. The cross-flow velocity was 0.9 m/s for both membranes, and the temperature used was 70°C during the experiment with the MPF 36 membrane and 80°C during the experiment with the NP010 membrane. The higher temperature used with the MPF 36 membrane in the concentration study (70°C) than in the parametric study (60°C) is due to the pressure-dependent maximum temperature of the MPF 36 membrane (Table 2). The experiment was interrupted at a volume reduction (VR) of 0.75, corresponding to a volume reduction factor (VRF) of 4. VR is defined as the ratio between the volume of the permeate and the initial volume of the feed. VRF is the ratio between the initial feed volume and the volume of the resulting retentate. The correlation between VRF and VR is:

$$VRF = \frac{1}{(1 - VR)} \tag{1}$$

The Microdyn-Nadir NP010 membrane was used in the concentration study in the DDS 20 module. The TMP was 15 bar, the cross-flow velocity was 0.9 m/s and the temperature was 80°C. NF was carried out to a VR of 0.93 (VRF 14) in the DDS module.

2.5. Analysis

The solids content was determined by weighing the sample before and after drying at 105°C. The ash content was determined by weighing the residue after heating to 575°C. The content of NaOH was then calculated from the ash content by multiplication with a correction factor of 1.29, as described previously [5]. The concentration of inorganic cations was determined by inductively coupled plasma atomic emission spectroscopy (ICP AES) with a Perkin Elmer (MA, USA) Optima 3000DV ICP AES instrument.

The concentration of sugars was determined by first degrading hemicellulose molecules to monomeric sugars using a standardized method for acid hydrolysis [13]. The concentration of the monomeric sugars D-galactose, D-glucose, D-xylose, D-mannose, and L-arabinose was then measured using high-performance anion-exchange chromatography coupled with pulsed amperometric detection [6].

The concentration of lignin was determined by measuring the UV absorbance at a wavelength of 280 nm in a spectrophotometer (UV-160, Shimadzu Corp., Kyoto, Japan). It should be noted that besides lignin, pectin degradation products have strong UV absorbance at 280 nm [14]. Thus, the presence of these substances could lead to an overestimation of the lignin concentration.

The molecular mass distribution of hemicelluloses and lignin was determined by size exclusion chromatography using a Waters 600E chromatography system (Waters, Milford, MA, USA) equipped with a refractive index detector (model 2414, Waters) and an ultraviolet detector operating at 280 nm (486, Waters). The analytical column was packed with 30 cm Superdex 30 and 30 cm Superdex 200 (GE Healthcare, Uppsala, Sweden). A 125 mM NaOH solution was used as eluent at a flow rate of 1 ml/min. The system was calibrated with polyethylene glycol (PEG) standards with peak molecular masses of 0.4, 4, 10 and 35 kDa (Merck Schuchardt OHG, Hohenbrunn, Germany).

3. Results

3.1. Parametric study

The influence of TMP and cross-flow velocity on the performance of seven membranes was studied in a parametric study. Experiments were performed at maximum temperature of the membranes from Pentair (40°C) and Koch (60°C), and at 80°C with the membranes from Tami and Microdyn-Nadir.

3.1.1. Effects on flux

MPF 36 is the more open of the two Koch membranes studied. The flux through this membrane was 470 l/m^2 h at a cross-flow velocity of 0.9 m/s and TMP of 15 bar, while the flux through the denser MPF 34 membrane was only 25 l/m^2 h under the same conditions. The influence of the cross-flow velocity on the flux through the MPF 36 membrane was significant, whereas the flux through the MPF 34 membrane was almost unaffected by the cross-flow velocity, as can be seen in Fig. 2a. The cross-flow velocity independency of flux of the MPF 34 membrane has also been observed by other researchers during NF of similar alkaline process solutions [10].

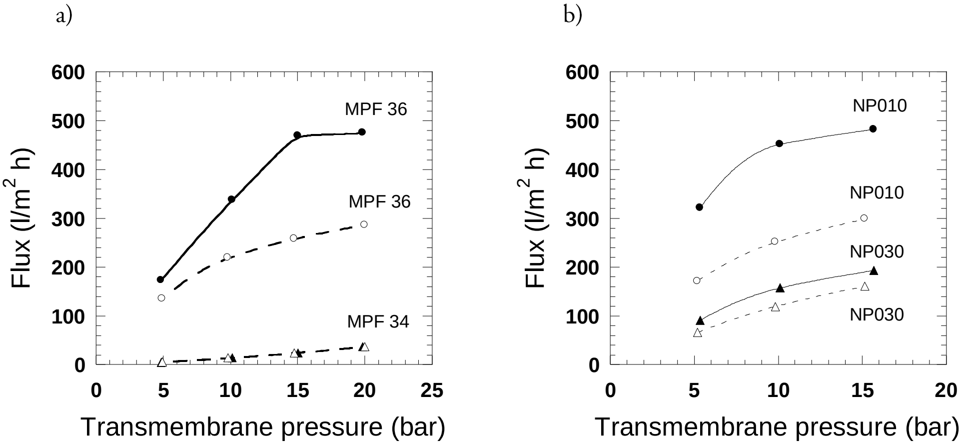


Fig. 2. Influence of transmembrane pressure on the flux of a) the two MPF membranes and b) the NP010 and NP030 membranes, at cross-flow velocities of 0.9 m/s (filled symbols) and 0.45 m/s (open symbols).

The flux of the more open Microdyn-Nadir membrane, NP010, was almost the same as that of the more open Koch membrane. The flux of NP010 was 480 l/m^2 h at 15 bar, while the flux of the denser NP030 membrane was only 190 l/m^2 h. As in the case of the two Koch membranes, the flux of the more open membrane was markedly higher at the higher cross-flow velocity, as shown in Fig. 2b. The marked influence of cross-flow velocity on flux for the two high-flux membranes MPF 36 and NP010 is presumably due to the more pronounced concentration polarization at high-flux conditions.

The flux through the hollow-fibre membranes manufactured by Pentair Inc. was unexpectedly high, already at relatively low TMP. The flux through the HFC 3 and HFR 2 membranes was 380 l/m^2 h, and 100 l/m^2 h, respectively, already at 5 bar. The flux was also independent of cross-flow velocity, as can be seen in Fig. 3a.

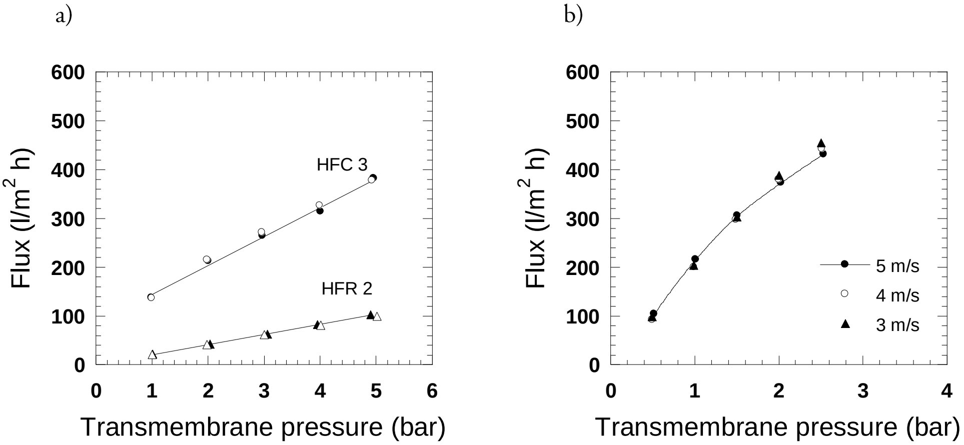


Fig. 3. Influence of transmembrane pressure on the flux of a) the two Pentair Inc. membranes at cross-flow velocities of 0.9 m/s (filled symbols) and 0.45 m/s (open symbols) and b) the Tami Inside membrane at three cross-flow velocities. Note the difference in the scales on the x-axis compared with Fig. 2.

The flux of the Tami membrane also increased rapidly with TMP and was 450 l/m^2 h already at 2.5 bar. The flux of this membrane was also independent of cross-flow velocity at the three velocities studied, as can be seen in Fig. 3b.

3.1.2. Retention of the NF membranes

As the objective of NF was to purify the NaOH solution, i.e. to retain all the components except NaOH, the retention (defined as one minus the ratio of the permeate concentration over the feed concentration) of NaOH must be low and the retention of lignin and sugars high. In Fig. 4 it is shown that the retention of sugars was >80%, and the retention of lignin >50% for four of the seven membranes investigated. The low retention of the HFR 2, HFC 3 and Tami membrane explains the high, and almost, linear TMP dependence of flux (see Fig. 3).

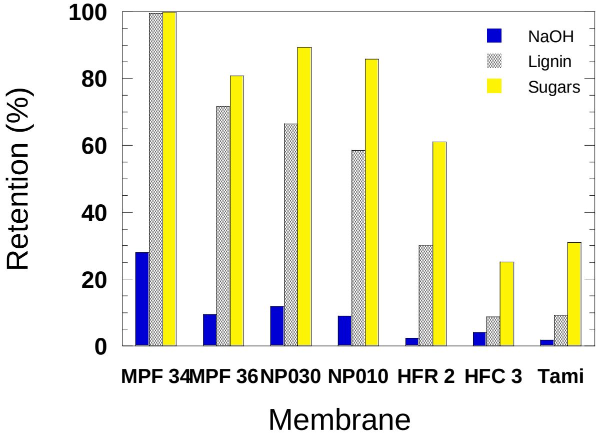


Fig. 4. Average retention of NaOH, sugars and lignin at the highest cross-flow velocity in the parametric studies shown in Figs. 2 and 3.

MPF 34 showed the highest retention of lignin and sugar, 99.5% and 99.9%. However, the retention of NaOH was also high, almost 30%, which means that the recovery of NaOH will be low. MPF 34 was considered to have too high retention of NaOH and too low flux to be useful in this application. However, this membrane has previously been used in harsh alkaline environments, for example, in the regeneration of caustic spent clean-in-place solutions in dairies [9]. If a very pure NF permeate is needed, this membrane is the natural candidate as it was the only one showing almost complete retention of lignin and sugar.

The retention of lignin and sugars by the MPF 36 membrane was somewhat lower, but the flux was markedly higher than for MPF 34. The retention of lignin and sugars by the Pentair and Tami membranes was too low for them to be suitable for this application. The retention of all three compounds by the NP030 and NP010 membranes was similar, but the flux of the NP010 membrane was markedly higher. MPF 36 and NP010 were thus considered to have the best performance and were further investigated in a concentration study.

3.2. Concentration study

3.2.1. Flux

The flux of the two membranes as a function of concentration (volume reduction) is shown in Fig. 5. The initial flux of the NP010 membrane was similar to that during the parametric study, whereas the initial flux of the MPF 36 membrane was lower due to the higher sugar concentration in the process solution used in the concentration study. The NP010 membrane showed a faster decline in flux with increasing VR. During concentration to a VR of 0.75, the average flux of the NP010 membrane was 205 l/m^2 h and that of the MPF 36 membrane 190 l/m^2 h.

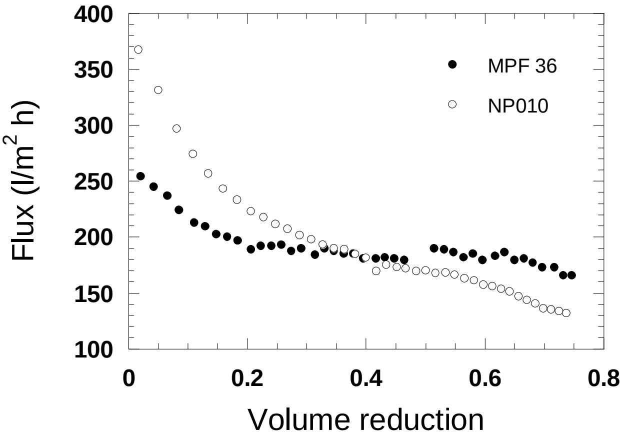
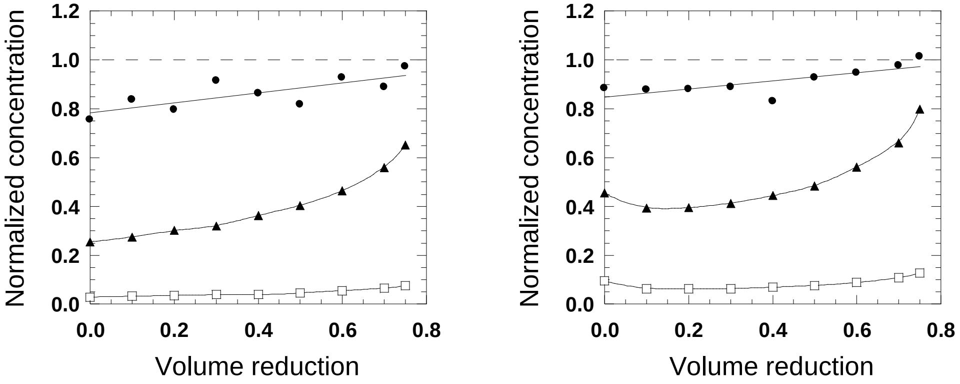


Fig. 5. Flux during concentration of process solution with the best two NF membranes. The cross-flow velocity was 0.9 m/s and the TMP was 15 bar. The temperature was 70°C (MPF 36) or 80°C (NP010).

3.2.2. Concentration in the permeate

The normalized concentration in the permeate (the ratio between the concentration in the permeate and the initial feed concentration) during VR is shown in Fig. 6. The concentration of NaOH was almost the same as in the feed and the concentration of sugars almost zero, whereas the normalized concentration of lignin was 0.26 (MPF 36) and 0.46 (NP010) initially, and increased with increasing VR. The mean retention of NaOH, lignin and sugars was 20%, 77% and 97%, respectively, for the MPF 36 membrane and 16%, 69% and 95%, respectively, for the NP010 membrane. The concentration of all three components in the permeate increased slightly during VR, as can be seen in Fig. 6. The concentration of NaOH in the permeate using the MPF 36 membrane was 36 g/l and in the permeate from the NP010 membrane 38 g/l, compared with 41 g/l in the feed.

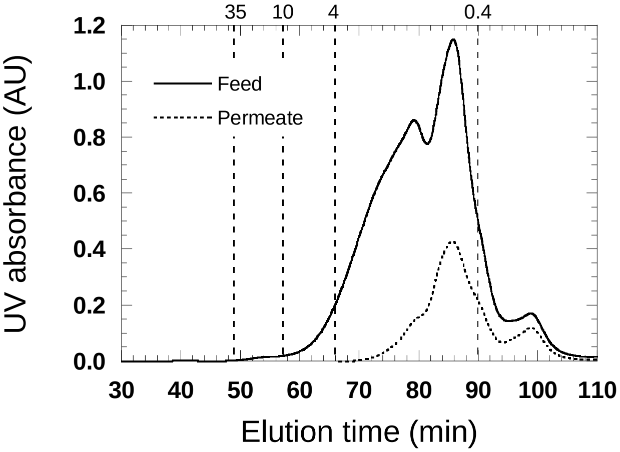

a)

b)

Fig. 6. Normalized concentration of NaOH (●), lignin (▲) and sugars (□) in the permeate using: a) the MPF 36 membrane and b) the NP010 membrane. The normalized concentration is the ratio between the concentration in the permeate and the concentration in the feed at VR 0.

The molecular mass of both lignin (measured as UV absorbance at 280 nm) and sugars (measured as refractive index) was lower in the NF permeate than in the feed, as shown in Fig. 7. No molecules larger than 4 kDa were found in the permeate, which means that high-molecular mass components were retained by the membrane.

a)



b)

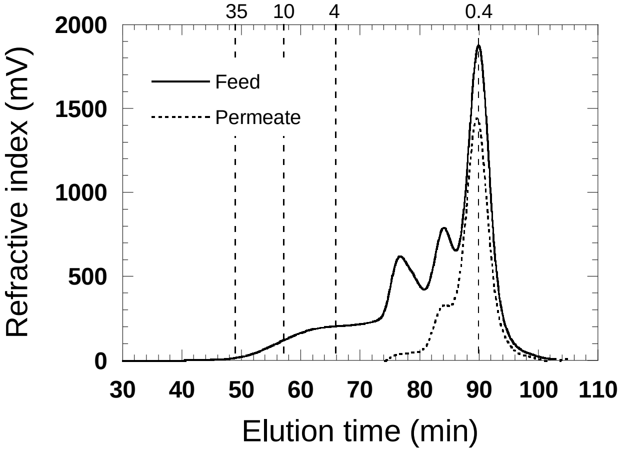


Fig. 7. Molecular mass distribution of a) lignin (measured as UV absorbance at 280 nm) and b) sugars (measured as refractive index) in the feed and permeate at the beginning of concentration using the Koch MPF 36 membrane. The vertical dashed lines indicate the molecular masses (kDa) of the PEG standards (given at the top of the figures).

4. Cost estimates

In order to reach higher VR than in the setup shown in Fig. 1, process solution was concentrated in a DDS 20 plate-and-frame module with the NP010 membrane from Microdyn-Nadir. The average flux was 206 l/m^2 h when concentrating to a VR of 0.93. The flux during concentration is shown in Fig. 8. A crystalline precipitate, found to contain mostly calcium when analysed by ICP AES, was observed in the cold retentate samples at concentrations above VR 0.8. A steep increase in ash content was observed at VR >0.8, which is also an indication of increased risk of scaling at higher VR. A maximum VR of 0.8 is therefore recommended in a commercial plant.

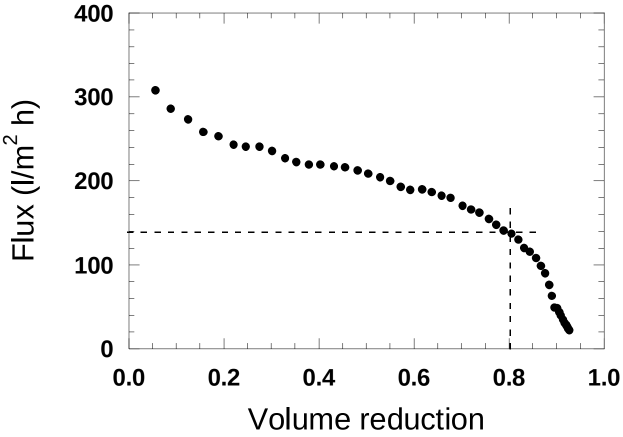


Fig. 8. Flux during concentration of process solution in a plate-and-frame module with the NP010 membrane from Microdyn-Nadir. The TMP was 15 bar, the cross-flow velocity 0.9 m/s, and the temperature 80°C. The dashed lines indicate the final VR recommended in a full-scale plant (0.8), and the flux at this VR (140 l/m^2 h).

The cost of an NF plant treating 10 m^3/h process solution was estimated based on the results of the concentration study and data obtained from membrane manufacturers. It was assumed that the plant will be equipped with a feed pump, a recirculation pump and a housing containing three spiral-wound membrane elements (Microdyn-Nadir OX-NP8040) in series with the NP010 membrane. It was also assumed that the plant will operate at a flux of 140 l/m^2 h, corresponding to the flux at the final VR (0.8). The experimental data used in the cost estimates are given in Table 3.

Table 3
Experimental data used in the cost estimates.

Feed flow (m^3/h)	10
Volume reduction	0.80
Flux (l/m^2 h)	140
Transmembrane pressure (bar)	15
Cross-flow in an element (m^3/h)	13.9*
Max. frictional pressure drop in an element at 80°C (bar)	0.5*
NaOH concentration in the NF permeate (g/l)	39

* Cross-flow and maximum frictional pressure drop for a Microdyn-Nadir 8040 membrane element

The membrane area of an 8040 membrane element with a 44 mil spacer is 27.5 m^2. The lifetime of the membranes was assumed to be 18 months if the plant is operated continuously. It was assumed that the membranes will be cleaned every second day during periods when the plant is in operation. The cost of cleaning with a commercial alkaline cleaning agent is 50 € per m^2 and year when cleaning every second day [15]. Maintenance and labour costs were estimated to be 2% of the investment cost [16]. The cost of NaOH is about 0.35 k€ per tonne when purchasing large amounts. The parameters included in the calculations are given in Table 4.

Table 4
Parameters included in the cost estimates.

Basic installation cost (€)	115 000
Membrane cost (less housing) (€/m^2)	95
Membrane area of a membrane element (m^2)	27.5
Membrane lifetime with full-time use (months)	18
Electricity price (€/kWh)	0.04
Pump efficiency	0.8
Cleaning cost (€/m^2 year)	50
Maintenance and labour cost (% of investment cost/year)	2
Cost of NaOH (k€/tonne)	0.35

4.1. Investment cost

The investment cost is composed of the cost of the basic plant and the cost of the membrane elements. The membrane area required, based on the flux obtained in the concentration study, is 57 m^2. The total membrane area of three 8040 membrane elements is 82.5 m^2, which allows both a lower flux than that achieved in this study, and daily cleaning of membranes, if necessary. The investment cost (including the first set of membranes) will be 123 k€.

4.2. Operating costs

The operating costs consist of electricity, replacement of membranes, cleaning, maintenance and labour costs. Electricity is needed mostly for pumping. A feed pump will be needed to deliver the inlet pressure of the plant and a recirculation pump will be needed to compensate for the frictional pressure drop and to maintain the circulation flow in the housing. The energy required per m^3 permeate in the feed pump is given by [15]:

$$W_{feed} = \frac{p_{inlet}}{\eta \cdot VR} \tag{2}$$

and in the recirculation pump:

$$W_{recirc} = \frac{\Delta p_f \cdot Q_{housing}}{\eta \cdot \left(J \cdot A_{housing}\right)} \tag{3}$$

where p_{inlet} is the inlet pressure to the plant, η is the pump efficiency, Δp_f and J are the frictional pressure drop and the flux in the housing, $Q_{housing}$ is the feed flow in the housing and $A_{housing}$ is the total membrane area in the housing. The energy required by the feed pump is thus 0.68 kWh/m^3 permeate and by the recirculation pump, 0.09 kWh/m^3.

The operating cost and the savings from the recovery of NaOH depend on the degree of use of the NF plant. Two scenarios were considered (see Table 5). In the first, it was assumed that the plant would be run continuously (8,000 h/year), and in the second only 25% of the time (2,000 h/year). The investment cost is the same in both scenarios (123 k€), but operating costs and savings are lower in alternative 2. The pay-back time will be less than two months if the plant is run continuously, and seven months when run at 25% capacity.

Table 5

Cost estimates for two scenarios: full-time use (8,000 h/y) and 25% use (2,000 h/y)

	Operating time (h/year)	
	8,000	2,000
NaOH recovered (tonne/year)	2,496	624
Savings due to recovery of NaOH (k€/year)	880	220
Operating costs (k€/year)	13.8	3.4
Electricity (k€/year)	2.0	0.5
Membrane replacement (k€/year)	5.2	1.3
Cleaning (k€/year)	4.1	1.0
Maintenance and labour (k€/year)	2.5	0.6
Pay-back time (months)	2	7

5. Conclusions

The alkaline extraction solution remaining after the recovery of hemicelluloses by UF can be purified by NF and reused for the extraction of biomass compounds. In this investigation a 4% NaOH solution used for the extraction of hemicelluloses in wheat bran was purified by NF. A preliminary cost estimate indicates a short pay-back time, although makeup with new NaOH will be needed as some NaOH will be retained by NF. However, the reduction in the cost of chemicals and discharge fees makes NF a promising method for the recovery of NaOH in alkaline extraction processes.

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References

[1] M.E.F. Bergmans, G. Beldman, H. Gruppen, A.G.J. Voragen, Optimization of the selective extraction of (glucurono)arabinoxylans from wheat bran: Use of barium and calcium hydroxide solutions at elevated temperatures, Cereal Science, 23:3 (1996) 235-245.

[2] M Bataillon, P Mathaly, A.-P Nunes Cardinali, F Duchiron, Extraction and purification of arabinoxylan from destarched wheat bran in a pilot scale, Industrial crops and products, 8:1 (1998) 37-43.

[3] W.G. Glasser, W.E. Kaar, R.K. Jain, J.E. Sealey, Isolation options for non-cellulosic heteropolysaccharides (HetPS), Cellulose, 7:3 (2000) 299-317.

[4] A. Höije, M. Gröndahl, K. Tømmeraas, P. Gatenholm, Isolation and characterization of physicochemical and material properties of arabinoxylans from barley husks, Carbohydrate Polymers, 61:3 (2005) 266-275.

[5] H. Krawczyk, A. Arkell, A.-S. Jönsson, Membrane performance during ultrafiltration of a high-viscosity solution containing hemicelluloses from wheat bran, Sep. Purif. Technol., 83 (2011) 144–150

[6] H. Krawczyk, A. Arkell, A.-S. Jönsson, Impact of prefiltration on membrane performance during isolation of hemicelluloses extracted from wheat bran, Sep. Purif. Technol., 116 (2013) 192–198.

[7] E. Sternemalm, A. Höije, P. Gatenholm, Effect of arabinose substitution on the material properties of arabinoxylan films, Carbohydrate Research, 343 (2008) 753-757.

[8] A.I. Yaich, U. Edlund, A.-C. Albertsson, Wood hydrolysate barriers: Performance controlled via selective recovery, Biomacromolecules, 13 (2012) 466-473.

[9] A.J. Mawson, Regeneration of cleaning and processing solutions using membrane technologies, Trends Food Sci. Technol., 8 (1997) 7–13.

[10] S. Novalic, A. Dabrovski, K.D. Kulbe, Nanofiltration of caustic and acidic cleaning solutions with high COD. Part 1. Recycling of sodium hydroxide, J. Food Eng., 38 (1998) 125–132.

[11] A. Bindoff, C.J. Davies, C.A. Kerr, C.A. Buckley, The nanofiltration and reuse of effluent from the caustic extraction stage of wood pulping, Desalination, 67 (1987) 455-465.

[12] R. Schlesinger, G. Götzinger, H. Sixta, A. Friedl, M. Harasek, Evaluation of alkali resistant nanofiltration membranes for the separation of hemicellulose from concentrated alkaline process liquors, Desalination, 192 (2006) 303-314.

[13] R. Ruiz, T. Ehrman, Laboratory analytical procedure LAP-014: Dilute acid hydrolysis procedure for determination of total sugars in the liquid fraction of process samples, NREL, Midwest Research Institute for the Department of Energy, USA, (1996)

[14] J. Konn, A. Pranovich, and B. Holmbom, Dissolution of fibre material in alkaline pre-treatment and refining of spruce CTMP, Holzforschung, 60 (2006) 32-39.

[15] A.-K. Nordin, A.-S. Jönsson, Influence of module configuration on total economics during ultrafiltration at high concentration, Chem. Eng. Res. Des., 88 (2010) 1555-1562.

[16] M. Cheryan M., Ultrafiltration and Microfiltration Handbook, Technomic Publishing. Co., Lancaster, USA, 1998.