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# Recovery of Hemicelluloses Extracted from Spruce and Wheat Bran

*Membrane Filtration Process Development and Cost Estimates*

Johan Thuvander  
Department of Chemical Engineering  
Lund University, Sweden  
2018



**LUND**  
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DOCTORAL THESIS

Academic thesis which, by due permission of the Faculty of Engineering of Lund University, Sweden, will be publicly defended on 6th April at 13:15 in Lecture Hall K:B at the Centre for Chemistry and Chemical Engineering, Naturvetarvägen 14, Lund

The faculty opponent will be Professor Mika Mänttari, Lappeenranta University of Technology, Finland

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*“If you can't do somethin' smart... do somethin' right.”*  
*- Jayne Cobb (Serenity, 2005)*

# Abstract

Hemicelluloses are a group of abundant polymers found in all plants and constitute about one third of the total plant biomass. These polymers can be used in many different products, such as oxygen barrier films, emulsifiers, foams and probiotic food additives. However, the commercial development and use of new products utilizing hemicelluloses has been limited due to the high production cost. Increased utilization of hemicelluloses would increase the value of biomass, and increase the proportions of products made from sustainable raw materials, and thus reduce our dependence on fossil materials.

In the work described in this thesis, hemicelluloses extracted from spruce and wheat bran have been recovered and purified using membrane filtration. As the molecular mass of the hemicelluloses was high, they were retained by the membrane, while water and low-molecular-mass contaminants, such as lignin, salt and sugar mono- and oligomers, passed through the membrane. This allows membrane filtration to be used for simultaneous concentration and purification of hemicelluloses.

In order for the membrane processes to be cost-effective, the filtration capacity, i.e., the flux, must be high. One problem associated with treating extracts from biomass is the adhesion of hydrophobic compounds onto the membrane surface, resulting in membrane fouling and thus reduced flux. However, these compounds can be removed by pretreating the extract. Various pretreatment methods have been investigated in attempts to obtain the highest possible flux.

Alkali-extracted wheat bran hemicelluloses, mainly arabinoxylan, were purified from contaminants such as suspended material, extraction chemicals and lignin. It was shown that the molecular mass of the hemicelluloses could be reduced by sparging the solution at 80 °C with air. This resulted in an almost fourfold increase in flux. The highest rate of flux increase was obtained when colloidal material had been removed from the solution by dead-end filtration prior to air sparging. Pretreating the solution with air sparging drastically decreased the cost of purifying the hemicelluloses by ultrafiltration and diafiltration.

The hemicelluloses recovered from process water after thermomechanical pulping of spruce, galactoglucomannan, were first purified using microfiltration to remove colloidal material. This had a significant positive effect on the filtration capacity of the subsequent hemicellulose recovery step using ultrafiltration. A pilot trial was conducted on-site at a thermomechanical pulp mill to evaluate the performance of the process. The results of this trial, combined with results from laboratory experiments, were used to estimate the cost of the membrane processes used for the recovery of the hemicelluloses from the process water. An additional benefit of

recovering dissolved hemicelluloses from the process water is that the cost of waste water treatment at the pulp mill will be reduced, which may compensate for part of the cost of the recovery of hemicelluloses.

# Populärvetenskaplig sammanfattning

En tredjedel av växtbaserad biomassa består av den naturliga polymeren hemicellulosa. Hemicellulosa utnyttjas idag inte till sin fulla potential, på grund av dyra uppreningskostnader. Eftersom hemicellulosa inte har kunnat utvinnas kostnadseffektivt så har produktutvecklingen av hemicellulosabaserade produkter hittills varit ytterst begränsad. Dock har man visat att hemicellulosa kan användas i flera produkter, så som syrgasbarriärer i livsmedelsförpackningar, dispersionsmedel, skum och som probiotiskt kosttillskott. Genom att ta till vara på denna utnyttjade råvara är det möjligt att skapa större värde av producerad biomassa, tillverka mer hållbara produkter och reducera användandet av fossila råvaror.

I detta arbete har hemicellulosa renats upp från två lösningar innehållande hemicellulosa utvunnen från biomassa. Den första lösningen var ett extrakt av vetekli, en biprodukt från tillverkningen av mjöl från vete. Den andra lösningen var processvatten från termomekanisk massatillverkning av granved, där hemicellulosan hittills har betraktats som en förorening i vattnet. Hemicellulosan koncentrerades och renades med hjälp av membranfiltrering. Membran är mycket täta filter som kan fraktionera molekyler i en lösning efter deras storlek. Hemicellulosan i detta arbete har varit mycket stora molekyler, vilket gör att de kan hållas tillbaka av ett membran samtidigt som vatten, salter och lignin kan passera, vilket leder till att hemicellulosan renas upp och koncentreras på samma gång.

För att hemicellulosa ska vara ett attraktivt råmaterial måste den kunna produceras på ett kostnadseffektivt sätt. På grund av detta måste membranprocesserna som används kunna filtrera en stor volym av lösning på kort tid. I detta arbete undersöktes inverkan av olika förbehandlingsmetoder, och hur det med hjälp av dessa är möjligt att göra lösningarna mer lättfiltrerade.

Genom att blåsa luft genom lösningen av vetekli vid 80 °C var det möjligt att höja filtreringshastigheten nästan fyrfaldigt. Genom att använda detta som förbehandlingsmetod var det möjligt att nästan halvera kostnaden för membranprocesserna som användes vid uppreningen av hemicellulosan.

Vid utvinning av hemicellulosa från processvatten från termomekanisk massatillverkning är det viktigt att kollodalt och suspenderat material tas bort innan hemicellulosan tas om hand med ultrafiltrering. I annat fall fastnar detta material på membranytan, vilket drastiskt sänker filtreringshastigheten. Med studier både utförda i labb och med en pilotanläggning på plats vid ett massabruk har kostnaden för membranprocesserna för uppreningen av hemicellulosa från det undersökta processvattnet uppskattats. Vid studierna på massabruket producerades

dessutom en större mängd hemicellulosa som nu kan användas vid utveckling av hemicellulosabaserade produkter. Ytterligare en bonus med utvinningen av hemicellulosa från processvatten är minskningen av energibehov och kemikalier vid massabrukets avloppsreningsverk, eftersom hemicellulosan utvinns och kan användas till värdefulla produkter istället för att hanteras som en förorening i vattnet.

# List of Publications

This thesis is based on the following publications, which will be referred to in the text by their Roman numerals.

- I. **Thuvander, J.**, Arkell, A. and Jönsson, A.-S.  
Centrifugation as pretreatment before ultrafiltration of hemicelluloses extracted from wheat bran. *Separation and Purification Technology*, 2014, 138, 1-6.
- II. **Thuvander, J.**, Arkell, A. and Jönsson, A.-S.  
Reduction of energy demand by use of air sparging during ultrafiltration of alkali-extracted wheat bran hemicelluloses, Submitted for publication.
- III. **Thuvander, J.**, and Jönsson, A.-S.  
Influence of air and nitrogen sparging on flux during ultrafiltration of hemicelluloses extracted from wheat bran, Submitted for publication.
- IV. **Thuvander, J.**, and Jönsson, A.-S.  
Techno-economic impact of air sparging prior to purification of alkaline extracted wheat bran hemicelluloses by membrane filtration, Manuscript.
- V. **Thuvander, J.** and Jönsson, A.-S.  
Extraction of galactoglucomannan from thermomechanical pulp mill process water by microfiltration and ultrafiltration – Influence of microfiltration membrane pore size on ultrafiltration performance. *Chemical Engineering Research and Design*, 2016, 105, 171-176.
- VI. **Thuvander, J.**, Zarebska, A., Hélix-Nielsen, C. and Jönsson, A.-S.  
Characterisation of irreversible fouling after ultrafiltration of thermomechanical pulp mill process water, *Journal of Wood Chemistry and Technology*, Accepted for publication.
- VII. **Thuvander, J.**, Lipnizki, F. and Jönsson, A.-S.  
On-site recovery of hemicelluloses from thermomechanical pulp mill process water by microfiltration and ultrafiltration, Manuscript.
- VIII. **Thuvander, J.**, Oinonen, P. and Jönsson, A.-S.  
Enzymatic treatment of hemicelluloses and lignin isolated from thermomechanical pulp mill process water. *Chemical Engineering Journal*, 2016, 296, 141-145.

## My Contributions to the Studies

- I. I performed the experiments together with Anders Arkell. I evaluated the results. The extraction of hemicelluloses was performed by our industrial partner. I wrote the paper together with the other authors.
- II. I performed the experiments and evaluated the results. The extraction of hemicelluloses was performed by our industrial partner. I wrote the paper together with the other authors.
- III. I planned the experiments and evaluated the results. Sandra Farran-Lee performed the experiments under my supervision. The extraction of hemicelluloses was performed by our industrial partner. I wrote the paper together with the other author.
- IV. I planned the experiments and wrote the paper together with the co-author. Sandra-Farran Lee performed the experiments under my supervision. The extraction of hemicelluloses was performed by our industrial partner. I evaluated the results.
- V. I planned the experiments and wrote the paper together with the co-author. I performed the experiments and evaluated the results.
- VI. I planned the experiments together with Ann-Sofi Jönsson. I performed the filtration experiments together with Josefin Bucht and Sandra Farran-Lee. I performed the determination of deposited polysaccharides on the membranes by acid hydrolysis, while Agata Zarebska performed and evaluated the data from the ATR-FTIR, SEM and EDS analysis. I wrote the paper together with the other authors.
- VII. I planned the experiments together with the other authors. I performed the experiments and evaluated the results. I wrote the paper together with the other authors.
- VIII. I planned the experiments together with Ann-Sofi Jönsson. I performed all the experiments, except the enzymatic treatment, which was performed by Petri Oinonen. I wrote the paper together with the other authors.

## Other related publications

- I. 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, 118, 387-393.

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# Abbreviations and Symbols

## Abbreviations

AX	Arabinoxylan
CFV	Cross-flow velocity
DF	Diafiltration
DMSO	Dimethyl sulfoxide
GGM	<i>O</i> -acetyl-galactoglucomannan
MF	Microfiltration
NF	Nanofiltration
NTU	Nephelometric turbidity units
RI	Refractive index
RO	Reverse osmosis
SEC	Size-exclusion chromatography
TMP	Thermomechanical pulp
UF	Ultrafiltration
UV	Ultraviolet
VR	Volume reduction

## Symbols

$c_b$	Concentration in bulk solution
$c_m$	Concentration at the membrane surface
$c_p$	Concentration in permeate
$D$	Mass diffusivity
$d_h$	Hydraulic diameter
$J$	Flux
$k$	mass transfer coefficient
$P_{feed}$	Pressure of feed

$P_{perm}$	Pressure of permeate
$P_{ret}$	Pressure of retentate
$R_a$	Resistance of adsorbed material
$R_{cp}$	Resistance of concentration polarization layer
$R_{fc}$	Resistance of filter cake
$R_m$	Membrane hydraulic resistance
$R_{ob}$	Observed retention
$R_{true}$	True retention
$Re$	Reynolds number
$Sc$	Schmidt number
$Sh$	Sherwood number
$V_{feed}$	Volume of feed
$V_{perm}$	Volume of permeate
$\Delta P$	Transmembrane pressure
$\Delta P_{avg}$	Average transmembrane pressure
$\mu$	Viscosity
$\Pi$	Osmotic pressure

# Contents

<b>1. Introduction .....</b>	<b>1</b>
1.1 Background .....	1
1.2 Aim and outline of this thesis.....	2
<b>2. Lignocellulosic Biomass .....</b>	<b>3</b>
2.1 Cellulose.....	3
2.2 Hemicelluloses .....	3
2.2.1 Spruce hemicelluloses .....	4
2.2.2 Wheat bran hemicelluloses.....	4
2.3 Lignin .....	5
2.4 Residual components.....	5
<b>3. Extraction of Hemicelluloses .....</b>	<b>7</b>
3.1 Alkaline extraction .....	7
3.2 Hot water extraction .....	8
3.3 Pulping .....	8
3.3.1 Kraft pulping .....	9
3.3.2 Sulphite pulping.....	9
3.3.3 Mechanical and thermomechanical pulping .....	9
3.4 Other methods .....	10
<b>4. Concentration and Purification of Hemicelluloses .....</b>	<b>11</b>
4.1 Centrifugation.....	11
4.2 Dead-end filtration .....	11
4.3 Precipitation .....	12
4.4 Membrane filtration.....	13
4.4.1 Diafiltration .....	13
4.5 Chromatography and adsorption .....	14
<b>5. Membrane Filtration.....</b>	<b>15</b>
5.1 Principles of membrane filtration.....	15
5.2 Membrane filtration parameters .....	16
5.3 Flux enhancement .....	19

5.3.1 Reduction of concentration polarisation.....	19
5.3.2 Feed pretreatment .....	21
5.4 Fouling and cleaning .....	22
5.4.1 Fouling.....	22
5.4.2 Cleaning.....	22
<b>6. Wheat Bran Arabinoxylan.....</b>	<b>23</b>
6.1 Solution containing extracted arabinoxylan .....	24
6.2 Pretreatment .....	25
6.2.1 Centrifugation and prefiltration .....	25
6.3 Gas sparging.....	29
6.3.1 Role of oxygen during gas sparing .....	31
6.4 Concentration and diafiltration.....	33
6.5 Cost estimates.....	35
6.6 Recovery of extraction chemicals .....	36
6.7 Final remarks on arabinoxylan recovery .....	37
<b>7. Spruce Galactoglucomannan.....</b>	<b>39</b>
7.1 Thermomechanical pulp mill process water.....	40
7.2 Prefiltration.....	41
7.3 Microfiltration .....	42
7.3.1 Influence of MF on UF performance.....	43
7.4 On-site pilot trial .....	46
7.4.1 Microfiltration .....	46
7.4.2 Ultrafiltration.....	47
7.4.3 Cost estimate .....	49
7.5 Impact of enzymatic lignin polymerization.....	50
7.6 Final remarks on galactoglucomannan recovery .....	52
<b>8. Conclusions and Future Work .....</b>	<b>53</b>
8.1 Arabinoxylan from wheat bran.....	53
8.2 Galactoglucomannan from spruce.....	54
<b>References .....</b>	<b>57</b>

# 1. Introduction

## 1.1 Background

Hemicelluloses are abundant plant polymers that typically constitute 20-40% of the biomass of common terrestrial plants [1]. These compounds can be utilized by either using, and possibly modifying, the natural hemicellulose polymers present in the plant matter, or by breaking them down into their basic building blocks and then using these to synthesize the desired products. The potential applications of products made from hemicelluloses are diverse, and include fuels [2, 3], organic acids [3], barrier films [3-5], foams [6], emulsifiers [3, 4] and probiotics [7, 8].

When processing biomass, it is necessary to separate and purify its individual constituents. Several methods can be used to dissolve the natural polymers in biomass. However, the resulting solution is usually dilute and contains impurities, and thus further processes are required to concentrate and purify the desired components. It is important that these separation processes are cost- and energy-efficient, as they often account for a large part of the capital and operating costs associated with chemical processes, being 60-80% in mature chemical processes [9] and 20-50% in biorefineries [10]. As price is an important factor if biobased materials are to compete with fossil-based materials, it is important that the separation processes are as cost-efficient as possible.

Membrane filtration is a cost- and energy-efficient separation process that separates components primarily according to their size. As dilute streams of non-volatile components will often have to be treated in biorefineries, where the size difference between different components may be large, it has been predicted that membrane filtration will play an important role in future biorefineries [10]. However, to enable the use of membrane filtration in these environments, additional knowledge must be obtained regarding the processes, in order to be able to manage membrane fouling and minimize costs.

## 1.2 Aim and outline of this thesis

The aim of the work presented in this thesis was to improve the recovery of hemicelluloses from alkali and water extracts using membrane filtration. Different extract pretreatment methods were used to increase the separation capacity and to reduce membrane fouling. The persistent foulants were characterized in order to improve our understanding of membrane fouling. Finally, cost estimates of the various processes involved in hemicellulose production were made based on the results from lab-scale experiments and an on-site pilot trial.

A brief overview of the different components of biomass is given in Chapter 2. Not only the different components are presented, but also which components are most abundant in the different types of biomass used. Chapter 3 describes how the hemicelluloses can be extracted from the biomass, and also provides an overview of the effects of the extraction method on the extracted hemicelluloses.

Methods that can be used for the concentration and purification of hemicelluloses are presented in Chapter 4. The main principles of membrane filtration, the central concentration and purification method used in this work, are covered in Chapter 5.

Chapter 6 presents the work carried out on the purification and concentration of the wheat bran hemicellulose arabinoxylan. Different pretreatment methods were explored in order to increase the flux, including dead-end filtration, centrifugation and air sparging. Arabinoxylan was purified with, and without, air sparging, and cost estimates were made for both cases to elucidate the economic impact of air sparging.

The studies carried out on the recovery of galactoglucomannan from thermomechanical pulp mill process water are presented in Chapter 7. Results from laboratory experiments and on-site pilot trials regarding the recovery of galactoglucomannan using microfiltration and ultrafiltration are presented.

Finally, the conclusions drawn from this work and recommendations for future studies are given in Chapter 8.

## 2. Lignocellulosic Biomass

Plants provide considerable sources of both materials and energy. The largest source of biomass in Sweden is forestry; the annual average growth of wood between 2012 and 2016 being 129 Mm<sup>3</sup> [11]. The agricultural sector is the second largest producer of biomass; for example, the production of wheat in Sweden in 2016 was 2.8 Mton [12]. Although agriculture focuses mainly on the production of food, several non-food by-products are produced. Straw and bran are, for example, by-products of wheat production.

The main components of plant biomass are the polymeric materials cellulose, hemicellulose and lignin. Plant biomass is therefore often referred to as lignocellulosic biomass, or simply “lignocellulose”. In addition, lignocellulosic materials also contain a range of minor components, such as extractives and inorganic salts, usually called “ash”.

### 2.1 Cellulose

Cellulose is the main structural polymer in lignocellulosic biomass. It is a straight polymer of  $\beta(1\rightarrow4)$  linked D-glucose subunits, often many thousands subunits long. Cellulose polymers bind to one another by hydrogen bonds, forming fibrils [13]. The fibrils are composed of both highly ordered cellulose polymers, forming crystalline regions, and less ordered regions, called amorphous cellulose. The combination of the high chain length of the cellulose and the high concentration of strong hydrogen bonds between the tightly packed cellulose polymers makes cellulose resistant to both dissolution and chemical degradation [14].

### 2.2 Hemicelluloses

Hemicelluloses are a diverse group of polysaccharides bound to the cellulose fibrils through hydrogen bonding, forming a layer around the fibrils that affords flexibility to the lignocellulosic structure [14]. Unlike cellulose, the hemicellulose polymer can be both linear and branched, and can be composed of multiple types

of sugar subunits, most commonly arabinose, galactose, glucose, xylose and mannose. The chain length of hemicelluloses is shorter than cellulose, and different side groups can be found on the sugar monomers. All these properties make hemicelluloses more susceptible to solubilisation and degradation [14].

### 2.2.1 Spruce hemicelluloses

The primary hemicelluloses in Norway spruce (*Picea abies*) are *O*-acetyl-galactoglucomannan (GGM), constituting 10-25% of the mass of spruce stemwood [4, 15]. The second most abundant hemicellulose, constituting 5-10% of wood, is arabinoglucuronoxylan [15]. In addition to these hemicelluloses, a wide range of hemicelluloses, such as arabinogalactan and  $\beta$ -glucan, are present at smaller amounts [15].

*O*-acetyl-galactoglucomannan is composed of a backbone of (1 $\rightarrow$ 4) linked  $\beta$ -D-mannose and  $\beta$ -D-glucose units. It contains side groups of  $\alpha$ -D-galactose units attached to some of the mannose in the backbone through (1 $\rightarrow$ 6) linkages [15, 16]. Additionally, part of the mannose units are *O*-acetylated at the C2 and C3 positions [15, 17]. The galactose side groups and acetyl groups contribute to the solubility of GGM [18]. The GGM family includes polysaccharides with different compositions. Softwood contains GGMs with high and low galactose contents, where the galactose:glucose:mannose ratios are typically about 1:1:3 and 0.1:1:3, respectively [16]. Due to the very low galactose content in low-galactose GGM it is sometimes referred to as glucomannan. The low content of galactose side groups on glucomannan means that its solubility is lower than that of high-galactose GGM [16].

Arabinoglucuronoxylan has a backbone of (1 $\rightarrow$ 4) linked  $\beta$ -D-xylose units, with side groups of 4-*O*-methyl- $\alpha$ -glucose and  $\alpha$ -L-arabinose at the C2 positions of the main chain [15].

### 2.2.2 Wheat bran hemicelluloses

Wheat bran is a by-product of the milling of wheat flour. It constitutes about 14% of the wheat kernel [19], and consists of 11-26% of the hemicellulose arabinoxylan [20] and minor amounts of  $\beta$ -glucan [21].

Arabinoxylan (AX) is composed of a backbone of (1 $\rightarrow$ 4) linked  $\beta$ -D-xylose units with 2-*O*- and/or 3-*O*-linked  $\alpha$ -D-arabinose side groups [22]. Furthermore, some of the arabinose side groups are 5-*O* linked with ferulic acid [23]. The ferulic acid residues are reactive and can bind hemicelluloses covalently by the reaction of two

ferulic acid groups, and bind to proteins [23], and affording AX anti-oxidant properties [24, 25].

## 2.3 Lignin

Lignin is made up of large cross-linked polyphenolic polymers consisting mainly of p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol monomers [26]. Lignin surrounds the cellulose fibrils, and can bind covalently to polysaccharides [27], giving lignocellulosic material additional strength and greater resistance to biological and environmental degradation [28].

The structure and composition of lignin vary between plant species and different parts of the plant. Softwood lignin is characterized by containing high amounts of coniferyl alcohol. The lignin in grasses contains all three lignin monomers, but contains more p-coumaryl alcohol than lignin from other sources [26].

## 2.4 Residual components

While cellulose, hemicellulose and lignin normally constitute most of the mass of lignocellulosic biomass, a wide range of other components are present in biomass. In some materials, these constitute only a minor fraction of the total mass, while in others they can make up a large part of the biomass structure. A selection of additional organic constituents of biomass are listed below.

- **Protein** – The protein content of biomass can vary greatly. Wheat bran has a relatively high protein content, 13-20% [25], while the protein content in softwood is low, 0.2-0.8% [29].
- **Pectin** – Pectic substances are polysaccharides similar to hemicelluloses, but are characterized by having a high amount of  $\alpha$ -D-galacturonic acid [30].
- **Extractives** – The extractives are composed of a large range of hydrophobic components such as fats, resins, sterols, terpenes [26] and lignan [31].

In addition to the organic components, lignocellulosic material also contains inorganic components that contribute to the ash content of the material. The ash is composed of the inorganic ions necessary for the biological function of the plants. The typical ash content in spruce wood is 0.4-3.2% and in wheat bran 3.5% [32].



## 3. Extraction of Hemicelluloses

The hemicelluloses are bound to the rest of the lignocellulosic material by both covalent linkages and by a high concentration of hydrogen bonds between the tightly packed polymers [15]. These bonds must be broken during extraction so that the hemicelluloses can be separated from the rest of the lignocellulosic material and purified. Several methods can be used to achieve this, which differ regarding extraction yield, selectivity and preservation of the native polymer structure.

### 3.1 Alkaline extraction

Papers I-IV describes the use of membrane filtration to concentrate and purify hemicelluloses extracted from wheat bran using alkaline extraction. Alkaline extraction of hemicelluloses from plant matter was used already in 1891 when Schulze coined the name “hemicelluloses” [33]. Although the definition of hemicelluloses has changed as our understanding of the structure of plant components has increased, alkali extraction is still widely used to solubilize hemicelluloses [34-39].

During alkaline extraction, the hydrogen bonds between the polysaccharide chains are broken due to the diffusion of cations into the material, causing it to swell, allowing lower-molecular-mass polymers to dissolve [2, 40]. Furthermore, the high pH will break ether bonds, releasing hemicelluloses bound to the lignin [41]. The high pH will also lead to the cleavage of arabinose, acetate [42-44] and phenolic side groups [25]. Cleavage of side groups can lead to reduced solubility of the polymer, and may cause the re-precipitation of hemicelluloses.

The use of elevated temperatures during extraction can increase the yield of extracted hemicelluloses [36]. However, at high temperatures the polysaccharide polymer starts to degrade. At 100 °C the primary kind of degradation is peeling reactions, where the polysaccharide chains are degraded from the reducing end [2, 45]. At higher temperatures, additional degradation takes place in the form of hydrolytic chain cleavage [2]. If the extraction yield is more important than a high molecular mass of the recovered hemicelluloses, an extraction process causing

partial degradation of the hemicelluloses can be used to obtain higher extraction yields due to the increase in solubility.

The solubility of hemicelluloses depends on the molecular mass, composition and structure of the hemicelluloses. Xylans are readily solubilized by alkaline extraction, whereas glucomannans is not as soluble in alkali alone. The yield of GGM using alkaline extraction can be improved by the addition of boric acid, which forms complexes with the hemicelluloses [46-48]. Furthermore, the hemicelluloses in grasses tend to be easier to extract than those in wood [49].

### 3.2 Hot water extraction

A lower consumption of chemicals during hemicellulose extraction can be achieved if the extraction is carried out using plain water. The yield of dissolved hemicelluloses in cold water is low, so higher temperatures are usually employed to increase the yield and shorten the required residence time [24, 34, 50, 51]. Due to the lower pH, it is possible to preserve the phenolic side groups on the polysaccharides to a greater extent with hot water extraction than with alkaline extraction [25]. However, high temperatures lead to the release of acetic acid from the biomass, causing acid hydrolysis of the polysaccharides [50]. This can increase the extraction yield, but reduces the molecular mass of the extracted hemicelluloses, which eventually will degrade into monomeric sugars [52]. Additionally, losses of arabinose side groups will occur at pH below 5 due to hydrolytic cleavage [53]. If high-molecular-mass hemicelluloses are desired, small amounts of sodium bicarbonate can be added to prevent deacetylation and degradation of the hemicelluloses [51].

### 3.3 Pulping

Pulping is the process of breaking down the lignocellulosic material into free fibres that can be suspended. The mass produced by pulping, called pulp, can then be used to produce paper and board [54]. This can be achieved by mechanical or chemical means, or by a combination of the two. Pulp is most commonly produced from wood, but other materials such as straw and bamboo can also be used [54].

### **3.3.1 Kraft pulping**

The most common pulping process is the kraft process [55]. During kraft pulping the wood chips are cooked with NaOH and Na<sub>2</sub>S at high temperature (160-180 °C) and pH (>12) [54]. The acetyl groups are cleaved at an early stage of the pulping process due to the high pH. The biomass is delignified by the cleavage of ether bonds within the lignin structure, reducing the molecular mass of the lignin and making it soluble in the high-pH solution [15]. Polysaccharides are degraded by peeling reactions at the reducing end, until stopped by the action of the competing stopping reaction converting the reducing end into a carboxylic acid group. The losses of GGM during kraft pulping of softwood can be greater than 70%, and of arabinoglucuronoxylan greater than 30% [15]. This is in contrast to alkaline extraction, where the xylans are more susceptible to solubilization than GGM. This difference is probably the result of a combination of different temperatures and extraction times, and the use of Na<sub>2</sub>S in kraft pulping.

### **3.3.2 Sulphite pulping**

When lignocellulose is cooked with sulphurous acids, and their alkali salts, lignin is solubilized by the actions of addition of sulphonate groups [54] and the cleavage of ether bonds [15]. Sulphite pulping can be carried out at a wide range of pH (1-13), limited by the solubility of the sulphite salts. When calcium is used, the pH must be below 2 to avoid calcium sulphite precipitation. When using magnesium, the pH can be increased to pH 5 and sodium places no limitation on the pH [15]. During low-pH sulphite pulping hemicelluloses are subjected depolymerization by acid hydrolysis. The side groups in the softwood hemicelluloses, GGM and arabinoglucuronoxylan are more sensitive to degradation and are cleaved off, leaving glucomannan and glucuronoxylan on the pulp fibres. During pulping, fragments of hemicelluloses are dissolved into the sulphite liquor, where they continue to be degraded over time into increasingly small fragments, and eventually into monomeric sugars. Several products can be extracted from the spent sulphite liquor, such as lignosulphonates, and the sugars can be fermented into ethanol.

### **3.3.3 Mechanical and thermomechanical pulping**

Papers V-VIII describe the recovery of hemicelluloses from thermomechanical pulp (TMP) mill process water. During thermomechanical pulping, the wood chips are pretreated with steam at about 120 °C, before being defibrated in a refiner [55]. Wood chips and water are fed into the refiner, where the fibres are liberated by

grinding between two metal discs. The temperature inside such a refiner can reach 180 °C [56], and one pass through the refiner typically takes only 3 seconds [57], after which the defibrated material is discharged and the temperature falls to around 80 °C. During thermomechanical pulping of spruce, 10% of the GGM present in the wood is dissolved in the process water [18], and the hemicelluloses obtained have relatively high molecular mass due to the short residence time in the refiner. However, to prevent problems caused by extractives during the papermaking process, large amounts of water are usually used to dilute the extractives and, consequentially, the extracted hemicelluloses are also diluted. Thus, large volumes of water have to be removed during the recovery of hemicelluloses from TMP mill processes water.

### 3.4 Other methods

It is possible to use organic solvents such as DMSO to dissolve hemicelluloses. In this way, it is possible to recover the hemicelluloses, while preserving their native acetyl groups. However, delignification of the material may be necessary before extraction [42]. When hypochlorite is used for delignification, the hemicelluloses obtained will have a smaller molecular mass [58].

The extraction of hemicelluloses can be assisted by various methods such as microwaves [59], ultrasound [60] and steam explosion [61]. The yield of extracted hemicelluloses can often be increased by increasing the severity factor (i.e., increasing the treatment time and/or temperature), however, the extracted hemicelluloses will have a lower molecular mass [62].

# 4. Concentration and Purification of Hemicelluloses

After the hemicelluloses have been liberated from the lignocellulosic biomass, the hemicellulose solution obtained is often dilute and contains many impurities. Typical contaminants are salts, lignin and extractives. In the case of alkaline extraction of hemicelluloses, the extraction chemicals must be recovered for reuse for good process economy, as discussed in Chapter 6.

## 4.1 Centrifugation

In the study described in Paper I, centrifugation was used as pretreatment before ultrafiltration (UF). Centrifugation is useful for the separation of fluids or suspended solids of different density. How well a fluid droplet or particle can be separated using centrifugation depends on its settling speed, which depends on the density of the solid and the liquid, the viscosity of the solution and the particle size. Centrifugation is widely used in industry for the removal of various types of solids from liquids, such as cream from skim milk, yeast from fermentation broth and pulp from fruit juice.

## 4.2 Dead-end filtration

Particles and suspended material, either contaminants or the precipitated product, can be removed by dead-end filtration. This was used in the studies described in Papers I-IV as pretreatment before UF. The material retained by the filter is accumulated on the filter surface, forming a filter cake. As the filter cake grows in thickness, the filtration resistance increases, requiring higher pressures to maintain the same filtration flow. When the filtration resistance becomes too high, the filter cake is removed and the filtration cycle restarted [63]. The filtration resistance of the filter cake depends on the size, shape and rigidity of the particles. If the filtration resistance is high it can be reduced by using a filter aid, consisting of

large hard particles that increase the porosity of the filter cake [63]. Dead-end filtration is used in numerous processes, including cell removal from fermentation broths, dewatering of ore slurries [64] and dewatering of precipitated lignin [65].

## 4.3 Precipitation

Hemicelluloses can be precipitated by neutralization, or the addition of an organic solvent or salt [66]. Different hemicelluloses precipitate under different conditions, meaning that solutions of hemicelluloses can be fractionated based on the choice of precipitation method. Selective precipitation by the formation of complexes can be achieved by exploiting the ability of some salts to form complexes with specific sugar monomers, or uronic acids.

After alkali extraction the hemicelluloses can be fractionated into water-soluble and water-insoluble hemicelluloses by neutralization of the solution. Methods of neutralization of the alkaline solution include the addition of an acid, or diafiltration (DF) (Paper IV).

The water-soluble hemicelluloses can be further fractionated by the addition of a miscible organic solvent (antisolvent), such as methanol, ethanol or acetone. The addition of an antisolvent changes the dielectric constant of the bulk solution, causing the precipitation of polymers [67]. Al-Rudainy et al. [67] also showed that the solutes could be fractionated into several distinct fractions of different polysaccharides and a lignin fraction by gradually adjusting the dielectric constant of spent sulphite liquor. The precipitate obtained from antisolvent precipitation contains concentrated hemicelluloses, with a reduced content of lipophilic extractives and lignin, as these components tend to remain in solution [68, 69]. It is also possible to fractionate the hemicelluloses according to size, as the hemicelluloses with the highest molecular mass precipitate first at the lowest addition of antisolvent [68]. Song et al. [69] compared membrane filtration to antisolvent precipitation of GGM and found that it was possible to obtain a purer GGM using antisolvent precipitation. However, they also concluded that membrane filtration might be more feasible on a larger scale, due to the large volumes of antisolvent that would be needed, or that membrane filtration could be used for preconcentration in order to reduce the volume of antisolvent required.

## 4.4 Membrane filtration

Hemicelluloses can be simultaneously concentrated and purified using membrane filtration by removing other solutes present after the extraction of the lignocellulosic biomass. Microfiltration (MF) membranes, whose large pores allow hemicelluloses to pass through, can be used to remove large, undesirable components such as particles and colloidal extractives [70, 71]. However, it has been reported that although the pores of MF membranes are considerably larger than the hemicellulose molecules, the retention of hemicelluloses during MF can be surprisingly high [37, 71, 72]. This was usually explained by the formation of secondary layers of material on the surface of the MF membrane.

Hemicelluloses can be concentrated using UF, and the feed volume can often be reduced by 80-99% [73]. The permeate from the concentration of the hemicelluloses can then be treated using a membrane with an even smaller pore size to remove low-molecular-mass contaminants, allowing the water or extraction solution to be reused [74].

One of the problems associated with the use of membrane filtration to fractionate components of lignocellulosic biomass is membrane fouling. Lignocellulosic biomass contains components with varying lipophilic properties, some of which become attached to the membranes, lowering the permeability. To address this problem, the membrane material [75, 76], mode of operation [77], cleaning conditions [78] and feed pretreatment [79] should be carefully considered when designing new processes using membrane filtration.

### 4.4.1 Diafiltration

During a special type of membrane filtration, DF, a solvent, usually pure water or a buffer solution, is added to the retentate at the same rate as permeate is withdrawn. As low-molecular-mass components pass through the membrane, while the large components are retained, the smaller components will be “washed out” of the retentate. However, one disadvantage of DF is that, high-molecular-mass components will also be lost if their retention is incomplete. Paper IV describes the use of DF to remove extraction chemicals from AX after initial UF concentration.

## 4.5 Chromatography and adsorption

Size-exclusion chromatography (SEC) exploits the differences in size of different solutes to purify hemicelluloses [66, 80]. Andersson et al. [80] used SEC to purify GGM from TMP mill process water. They found that it was possible to obtain a GGM with a purity of 80% at high yields. However, they concluded that DF would probably be a cheaper method of purification. Another disadvantage of SEC is that the concentration of the product is low, requiring additional processing to increase the concentration of the hemicelluloses.

Neutral and acidic polysaccharides can be fractionated using anion-exchange chromatography [66], in which diethyl aminoethyl cellulose resin is often used, together with gradients of borate, NaOH or NaCl.

Adsorption can be used to remove hydrophobic contaminants such as lignin, lignin-carbohydrate complexes and other extractives [75, 79, 81, 82]. Although this method does not increase the concentration of hemicelluloses, it is possible to remove contaminants that are either harmful in downstream processing [79], or are valuable in their own right [75, 79].

# 5. Membrane Filtration

## 5.1 Principles of membrane filtration

Pressure-driven membrane processes, in which the feed solution is pressurized and fed over a semi-permeable membrane, are the class of membrane processes closest to traditional filtration. The solvent, and substances smaller than the pores, will pass through the membrane, forming the “permeate”, while the components in the feed that are larger than the pores are retained, forming the “retentate”, as illustrated in Figure 1. During traditional dead-end filtration, the retained material will accumulate on the surface of the filter and form a filter cake that will increase in thickness as filtration proceeds. The accumulation of material the surface during filtration can be reduced by pumping the feed tangentially onto the filter surface, in a process called cross-flow filtration. The flow of the fluid flushes away material from the filter surface, which leaves the module with the retentate.

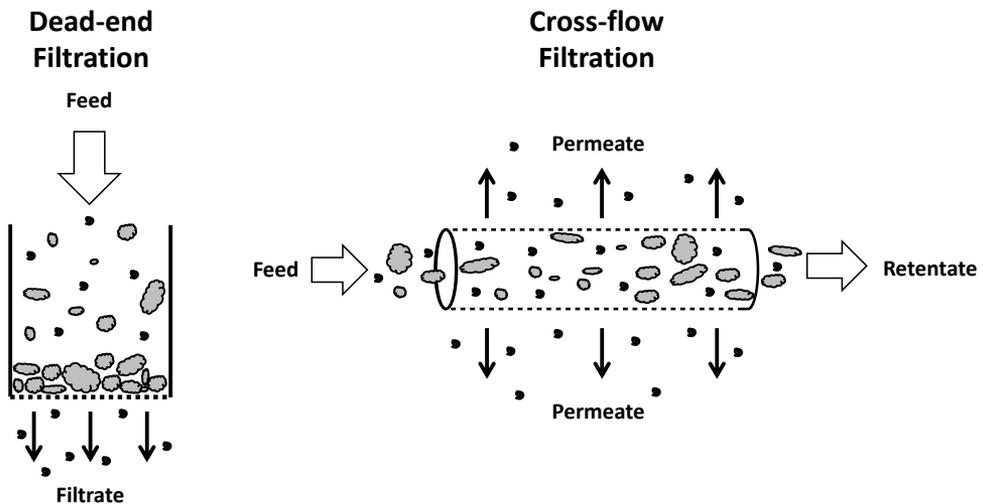


Figure 1. Schematics of dead-end filtration (left) and cross flow filtration (right).

The pressure-driven membrane filtration processes are MF, UF, nanofiltration (NF) and reverse osmosis (RO). MF membranes are the most open, allowing even

relatively large components to pass through, while RO retains small components, including ions. These kinds of membrane filtration are not well defined, and overlap to some degree, as can be seen from Table 1, as they were historically defined according to application rather than membrane characteristics.

**Table 1.** Typical process conditions and characteristics of pressure driven membrane processes [73, 83]

	<b>Operating pressure (bar)</b>	<b>Pore size (nm)</b>	<b>Nominal molecular weight cut off (Da)</b>	<b>Application</b>
<b>MF</b>	<2	>100	-	Cell separation
<b>UF</b>	1-10	1-100	>1000	Protein and polysaccharide purification
<b>NF</b>	3-40	~1	200-1000	Water softening
<b>RO</b>	10-100	-	<200	Desalination

## 5.2 Membrane filtration parameters

The performance of a membrane filtration process is dependent on a range of parameters derived from the properties of the membrane and the feed, and the operating parameters. These parameters will affect the rate at which permeate is produced, the flux ( $J$ ), and how well the membrane retains the material of interest, i.e., the retention. During the filtration of a pure solvent, or during filtration under conditions without the enrichment of retained material at the membrane surface, the flux will increase linearly with the pressure difference across the membrane, i.e., the transmembrane pressure ( $\Delta P$ ) [84].

$$J = \frac{\Delta P}{R_m \cdot \mu} \quad (5.1)$$

$R_m$  is the filtration resistance of the membrane and  $\mu$  is the viscosity of the permeate.

The value of  $\Delta P$  varies locally in a membrane module. While the pressure on the permeate side,  $P_{perm}$ , is usually fairly constant, the pressure of the feed at the inlet,  $P_{feed}$ , will be higher than at the outlet,  $P_{ret}$ , due to frictional pressure drop. This will result in a higher value of  $\Delta P$  at the beginning of the membrane module than at the end. The value of  $\Delta P$  is often given as the average transmembrane pressure  $\Delta P_{avg}$  in the module (Equation 5.2).

$$\Delta P_{avg} = \frac{P_{feed} + P_{ret}}{2} - P_{perm} \quad (5.2)$$

At high cross-flow velocity (CFV), or in long modules, the frictional pressure drop can exceed half of the transmembrane pressure. When this happens, the flux will be reversed at the end of the membrane module, and some of the permeate will be lost [85], as illustrated in Figure 2. This effect was observed in the study presented in Paper II, where lower fluxes were obtained at low transmembrane pressure and at high CFV.

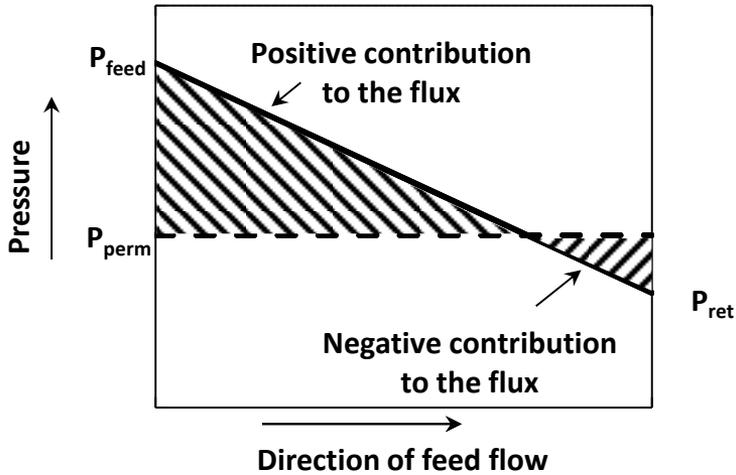


Figure 2. Illustration of the change in transmembrane pressure along a membrane module.

During the filtration of a solution containing substances that are retained by the membrane, the concentration of the retained material at the membrane surface,  $c_m$ , will increase and be higher than the concentration in the bulk solution,  $c_b$ , as illustrated in Figure 3. Eventually, a concentration gradient will develop as equilibrium is established between the convective forces forcing material towards the membrane surface, and the back-diffusion of this material. This gradient, called the concentration polarisation, will create an additional resistance to filtration, which is expressed by an extra resistance factor ( $R_{cp}$ ).

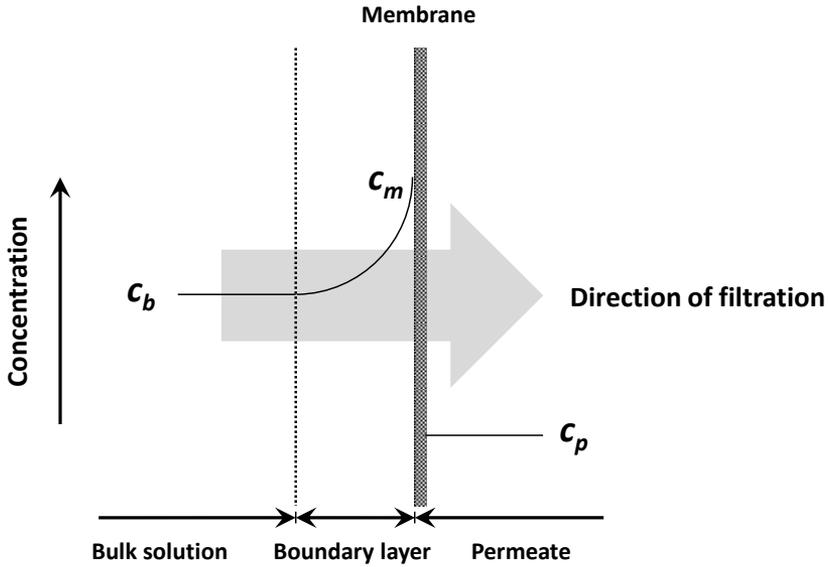


Figure 3. Illustration of concentration polarisation during membrane filtration.

Additional resistance factors can be added to account for different types of phenomena that reduce the rate of filtration, such as the resistance due to the filter cake ( $R_{fc}$ ) or adsorbed material ( $R_a$ ). The driving force can also be decreased by a difference in osmotic pressure ( $\Pi$ ) between the membrane surface and the permeate [84]. Equation 5.3 shows how these parameters affect the flux. In real systems these parameters are likely to change over time. It is common for fouling to build up over time, increasing  $R_{fc}$  and  $R_a$ .

$$J = \frac{\Delta P - \Pi}{(R_m + R_{cp} + R_{fc} + R_a) \cdot \mu} \quad (5.3)$$

The true retention,  $R_{true}$ , is determined from the difference in  $c_m$ , and the concentration in the permeate,  $c_p$ :

$$R_{true} = 1 - \frac{c_p}{c_m} \quad (5.4)$$

However,  $c_m$  cannot usually be measured during normal operation and the observed retention,  $R_{obs}$ , is used instead of the true retention, which depends instead on  $c_b$ :

$$R_{obs} = 1 - \frac{c_p}{c_b} \quad (5.5)$$

$R_{obs}$  can decrease if the concentration at the membrane surface is increased by an increase in flux, while  $R_{true}$  remains constant.

During concentration, the volume of the feed,  $V_{feed}$ , will decrease as the permeate is withdrawn. The volume reduction (VR) is used to measure of how much of the initial feed volume has been withdrawn as permeate,  $V_{perm}$ :

$$VR = \frac{V_{perm}}{V_{feed}} \quad (5.6)$$

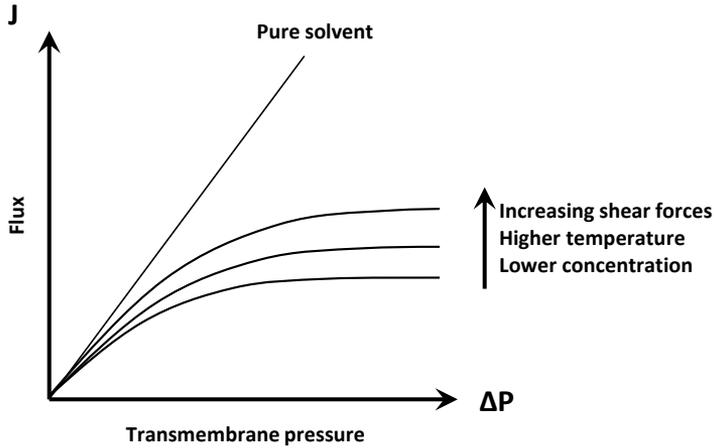
The concentration of retained material in the retentate will increase with increasing VR. This will increase the viscosity of the retentate and thus the concentration at the membrane surface, resulting in a lower flux. Eventually, the flux will have decreased until it is unfeasible to proceed any further.

## 5.3 Flux enhancement

A high flux is important in order to reduce the membrane area required, the energy demand and the production cost. Several measures can be taken to maintain a high filtration capacity, including feed pretreatment and changing the process parameters. These measures are often associated with additional costs, which must be weighed against the reduced capital and energy costs associated with a higher flux.

### 5.3.1 Reduction of concentration polarisation

As the resistance to filtration increases at increasing transmembrane pressure, the flux will eventually level off at the limiting flux. The limiting flux can be increased by increasing the transport of material away from the membrane surface, as illustrated in Figure 4.



**Figure 4.** Illustration of flux as a function of transmembrane pressure when filtering a pure solvent or a solution with material retained by the membrane.

The concentration polarisation and the formation of a filter cake can be reduced in several ways, for example, by increasing the shear forces at the membrane surface. The shear stress can be increased by increasing the CFV. However, this will increase the energy demand and the frictional pressure drop. If low transmembrane pressures or long membrane modules are to be used, the frictional pressure drop limits the CFV that can be used before negative transmembrane pressure and reversed flux are observed at the end of the module [85, 86]. Other means of increasing the shear forces at the membrane surface are to use vibrating or rotating modules [84].

Increasing the temperature also has positive effects on the flux, due to both lower permeate viscosity and faster back-diffusion of retained substances at the membrane surface. However, the maximum temperature may be limited by the thermal stability of the membrane and product.

The flux in the pressure-independent mass transfer region is given by the film model equation:

$$J = k \cdot \ln \left( \frac{C_m - C_b}{C_b - C_p} \right) \quad (5.7)$$

where  $k$  is the mass transfer coefficient. The mass transfer coefficient is related to the operating conditions in the system by the dimensionless correlation between the Sherwood number ( $Sh$ ), the Reynolds number ( $Re$ ) and the Schmidt number ( $Sc$ ).

$$Sh = \frac{k \cdot d_h}{D} = a \cdot Re^b \cdot Sc^c \quad (5.7)$$

Where  $d_h$  is the characteristic length (m) and  $D$  the mass diffusivity ( $\text{m}^2/\text{s}$ ). Typical values for the coefficients  $a$  and  $b$  are 1.86 and 0.33 during laminar flow, and 0.023 and 0.8 during turbulent flow. The value of  $c$  is 0.33 during both laminar and turbulent flow [84].

The concentration polarisation layer can be disturbed and deposited material can be removed by temporarily reversing the permeate flow, i.e., back-pulsing and back-flushing. Back-pulsing is the use of frequent short pulses, while back flushing is usually performed less frequently, using a larger volume of permeate to flush the membrane. Both ceramic tubular membranes and hollow-fibre membranes are suitable for back-pulsing, while there is a risk of delamination of the active membrane layer if the permeate flow is reversed in polymeric flat sheet membranes. It has been reported that back-pulsing, by enabling a reduction of the CFV while maintaining production capacity, reduced the energy consumption by 50% during MF of skim milk [77].

Finally, shear forces can be increased, and flow profiles disturbed by inducing a two-phase flow by injecting gas into the liquid feed. The two-phase flow will increase the mass transport [87] of material away from the membrane surface. Gas sparging has been shown to increase the flux during the filtration of many components, including dextran [88, 89] and yeast [90, 91]. Gas sparging can be used to reduce membrane fouling through the increased turbulence at the membrane surface. This has become a widely adopted method for fouling control during the operation of membrane bioreactors [92]. The influence of gas sparging during UF of alkaline wheat bran AX was investigated in this work (Papers II-IV).

### **5.3.2 Feed pretreatment**

Untreated feeds often contain substances that will cause problems during processing, such as membrane fouling, feed channel blockage and enrichment of contaminants. Prefiltration using either dead-end filtration or a more open membrane can be used to remove particles and colloidal material. In the studies described in Papers V and VI it is shown how the removal of colloidal matter dramatically increased the UF flux and reduced membrane fouling. Other types of pretreatment include the removal of foulants by adsorption [75, 79] or oxidative degradation [93]. The use of oxidation to reduce feed viscosity, and thus increase the flux, is discussed in Papers III and IV.

## 5.4 Fouling and cleaning

The accumulation of foulants on the membrane surface and within the pores during filtration will increase the filtration resistance, reducing the flux and changing the selectivity of the membrane. The membrane flux must therefore be restored periodically by cleaning. The appropriate cleaning method depends on the foulants.

### 5.4.1 Fouling

Several mechanisms are responsible for membrane fouling: adsorption of material in the pores of the membrane, plugging of the pores, cake formation on the surface of the membrane [84], and precipitation of inorganic substances on the membrane surface (scaling) [94].

During the filtration of water from the pulping industry, the membranes can be fouled by hydrophobic extractives [95, 96], polysaccharides [97] and lignin [98]. Paper VI describes a study in which the components of the persistent fouling of UF membranes by TMP mill process water were investigated.

### 5.4.2 Cleaning

Membranes can be cleaned using a wide range of cleaning agents, consisting of mixtures of alkali, acids, enzymes, tensides and oxidizing agents. The cleaning costs and process downtime should be reduced by tailoring the membrane cleaning procedure to the foulants encountered in each specific application. Proteins and other organic foulants [84] are usually effectively removed by alkaline cleaning agents while inorganic material is more effectively removed using acid cleaning agents [84]. Oxidizing agents, such as chlorine, hydrogen peroxide and peracetic acid are commonly used for equipment disinfection but can also remove deposited material by degrading it and making it more soluble [99]. Enzymes can be used when the membrane has been fouled by a specific known substance, and are used to clean membranes fouled by whey proteins [100].

## 6. Wheat Bran Arabinoxylan

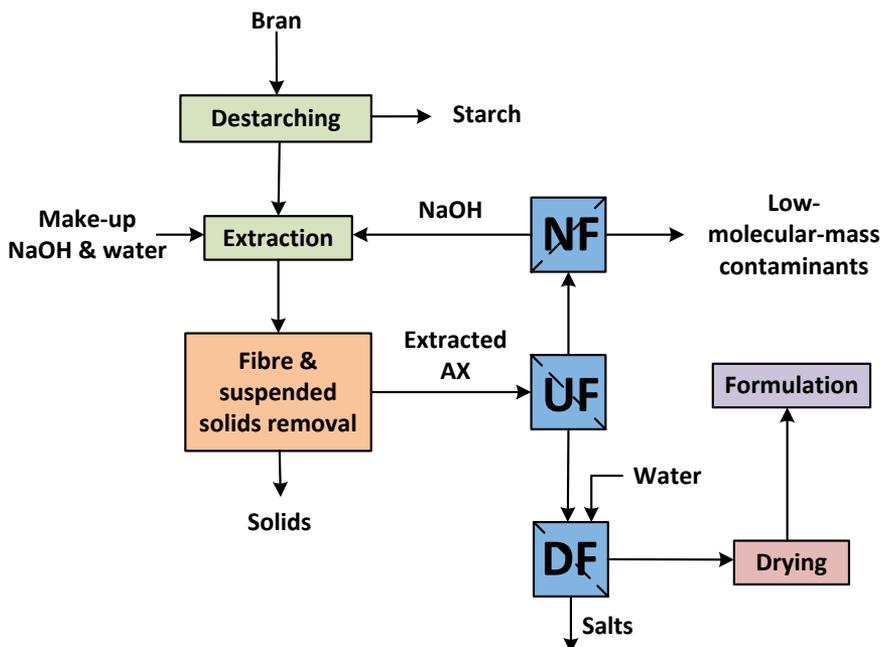
Steiger and Schulze presented evidence of hemicelluloses in wheat bran over a century ago by demonstrating the presence of pentose sugars [101]. Forty years later, in 1930, Norris and Preece showed that wheat bran hemicelluloses could be fractionated into several fractions with different chemical compositions and properties [102]. Since then, several processes have been proposed for the isolation of the main wheat bran hemicellulose, AX, utilizing various methods, including alkaline [34, 37, 103], water [24, 25], ultrasound [60], microwave [104] and enzyme [105] extraction. The extraction method used determines the properties of the extracted compounds. Microwave treatment and enzymatic extraction can cause severe degradation of the hemicellulose polymer, yielding mainly mono- and oligosaccharides. Higher-molecular-mass polymers are obtained using hot water extraction or alkaline extraction. When using hot water extraction, it is possible to obtain polymeric AX with preserved ferulic acid side groups, while a higher AX yield is obtained with alkaline extraction, but without the ferulic acid side groups [25].

Most of the large-scale extractions of polymeric AX have been conducted using the alkaline extraction method [34, 37, 103, 106], probably due to the higher AX yield. The alkaline AX solution is viscous and, besides AX, contains mainly the extraction chemicals and small amounts of lignin [107]. Several methods have been used to purify AX from the various contaminants. Antisolvent precipitation is one of the most common purification methods on laboratory scale. Large-scale extraction would require the handling of large amounts of antisolvent, and it is thus common to use membrane filtration to concentrate the AX before either precipitation or drying of the AX. However, due to the high viscosity of the alkaline hemicellulose solution, the resulting UF flux is low [103, 107, 108]. It has been shown that the UF flux can be increased by increasing the temperature and CFV [107], and by pretreatment using dead-end filtration [72].

In this work the purification of alkali-extracted wheat bran AX using UF was studied. A simplified overview of the process used for extraction and purification of the wheat bran AX is shown in Figure 5. The AX was extracted from destarched wheat bran using NaOH, and the solution containing the extracted AX was supplied by an industrial partner. Pretreatment by centrifugation and dead-end filtration was studied as a means of improving the UF flux (Paper I). The influence

of air sparging, and the role of oxygen on the molecular mass reduction of the AX and on the UF flux was also investigated (Papers III and IV). The cost of the recovery and purification of AX using membrane filtration was estimated, and the influence of air sparging on the cost was investigated (Paper IV).

A large amount of NaOH is required for AX extraction. At least partial recovery of the NaOH would probably be necessary for an economically feasible process. The possibility of using NF to purify the spent NaOH solution was therefore investigated in a previous study [74].



**Figure 5.** Schematic representation of the extraction and purification of hemicelluloses from wheat bran.

## 6.1 Solution containing extracted arabinoxylan

After the AX extraction, the solid fraction, consisting mainly of cellulose, was removed using a nozzle separator (Clara 20 low flow nozzle separator, Alfa Laval, Sweden). The typical composition of the extract is given in Table 2. The main component is the NaOH used to extract the AX from the wheat bran, typically at a concentration of 30-40 g/L. The content of hemicelluloses was around 7 g/L, consisting mainly of AX and minor amounts of hemicelluloses consisting of galactose and glucose. The amount of lignin was about 2 g/L lignin.

**Table 2.** Concentration of constituents in the three batches of unfiltered AX solution used in the studies in Paper I and III

	<b>Concentration (g/L)</b>	
<b>Total dry solids</b>	46.0	± 3.4
<b>NaOH</b>	36.5	± 4.0
<b>Hemicelluloses</b>	7.5	± 0.5
- Arabinan	1.9	± 0.2
- Galactan	0.2	± 0.1
- Glucan	1.2	± 0.3
- Xylan	4.2	± 0.5
<b>Acid-soluble lignin</b>	2.5	± 0.4
<b>Acid-insoluble lignin</b>	0.25	± 0.1

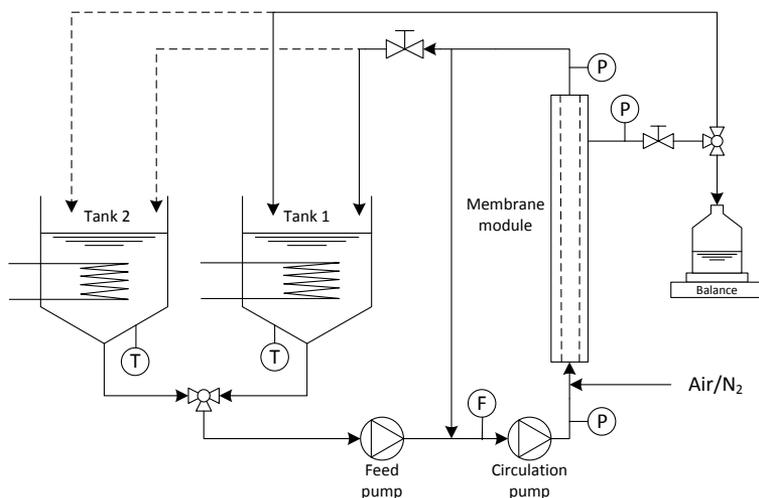
## 6.2 Pretreatment

After the solid fraction has been removed using the nozzle separator, a crude AX solution is obtained. This solution still contains suspended matter, making the solution slightly turbid in appearance. If no further pretreatment is applied, the subsequent UF flux will be low [107], resulting in a high cost of purification of the AX. Furthermore, pretreatment of the solution may be necessary to improve the product properties. Particulate material present in the solution will be retained and concentrated together with the hemicelluloses if not removed prior to UF, which may have a detrimental effect on the final product. Furthermore, the viscosity of the solution should be considered. If the intended final product is a concentrated aqueous solution, an excessively high viscosity may be undesirable.

### 6.2.1 Centrifugation and prefiltration

The turbidity of the solution gives an indication of the amount of colloidal material present. Turbidity measurements on different batches showed considerable variation between the batches. The turbidity of the hemicellulose solution has also been found to be correlated with solution viscosity, 340 NTU and 2.7 mPa·s in Paper I and 690 NTU and 4.8 mPa·s [72]. In order to remove colloidal material and reduce the viscosity, the crude solution was pretreated using various combinations of centrifugation and dead-end filtration. The effect of the pretreatment was then evaluated in the UF set-up shown in Figure 6. The set-up consists of two 200 L tanks, a feed pump, a recirculation pump and a membrane module. The membrane used was a ceramic tubular membrane with a molecular mass cut-off of 10 kDa, made of Al<sub>2</sub>O<sub>3</sub> with an active layer of TiO<sub>2</sub>

(Atech innovation GmbH, Gladbeck, Germany). The retentate and permeate were recirculated during the UF studies, and the outlet of the retentate recirculated back to tank 1 was located *above* the liquid surface. (For further details, see Paper I.)

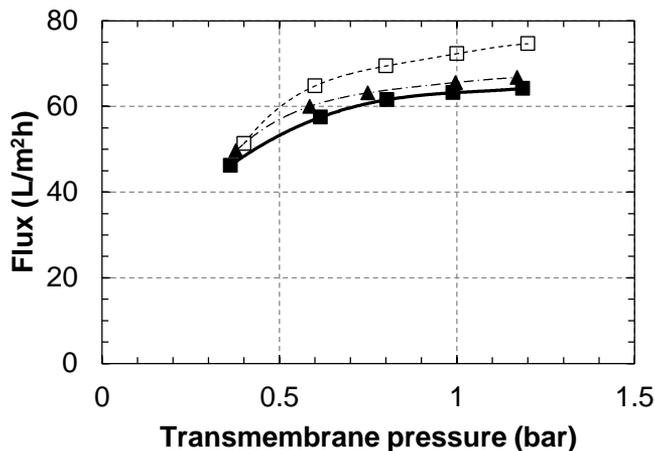


**Figure 6.** UF filtration set up used in the study on centrifugation and dead-end filtration pretreatment described in Paper I. Note that the retentate outlet was positioned above the liquid surface.

The effect of centrifugation was initially studied by varying the residence time in the nozzle separator used for the removal of the solid residue. The residence time was increased by reducing the flow through the separator from 300 L/h to 65 L/h. This resulted in a reduction in turbidity of the solution from 340 NTU to 270 NTU, with a corresponding decrease in viscosity at 80 °C from 2.7 mPa·s to 1.9 mPa·s. It is thus possible to reduce the amount of suspended material in the solution by increasing the residence time in the nozzle separator. However, only a minor increase in flux, from 64 L/m<sup>2</sup>h to 67 L/m<sup>2</sup>h was observed during UF at a transmembrane pressure of 1.2 bar, a CFV of 4 m/s and a temperature of 80°C, as can be seen in Figure 7.

The turbidity of the solution was further reduced by pretreatment with high-speed centrifugation, by increasing the time of centrifugation and gravitational force. After the longest time and highest gravitational force (15 min, 30 000 g) the turbidity of the solution had decreased from 550 NTU to 100 NTU. The viscosity initially decreased quickly using high-speed centrifugation. After 5 min of centrifugation, the viscosity at 80 °C decreased from 3.6 mPa·s to 2.79, 2.69 and 2.6 mPa·s at 10 000 g, 20 000 g and 30 000 g, respectively. Increasing the duration of high-speed centrifugation did not improve the viscosity significantly, and the viscosity after 15 min of high-speed centrifugation was 2.6 mPa·s at all gravitational forces studied.

A larger volume of solution was centrifuged at 30 000 g, for 15 min. UF of the high-speed-centrifuged solution showed only minor improvements in flux, as can be seen in Figure 7, increasing to 74 L/m<sup>2</sup>h at a transmembrane pressure of 1.2 bar, a CFV of 4 m/s and a temperature of 80 °C.



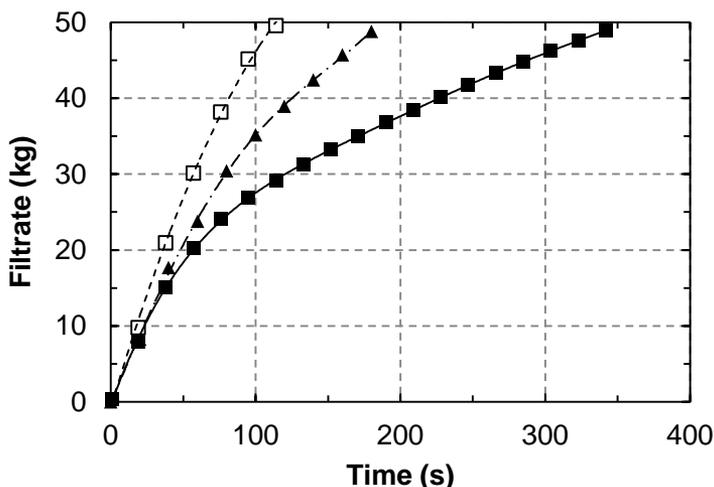
**Figure 7.** Flux during UF at 80 °C and CFV of 4 m/s. Untreated solution (■). Solution treated with long residence time in the nozzle separator (▲). Solution treated with high-speed-centrifugation (□). (From Paper I)

Krawczyk et al. [72] showed that prefiltration of the hemicellulose solution drastically improved the UF flux. However, they used a large amount of diatomaceous earth as filter aid: i.e., 2 wt%, which can be compared with the clarification of beer, where the typical amount of filter aid is only 0.1-0.2 wt% [109]. Improving the filtration properties of the solution would thus reduce the amount of filter aid required for the prefiltration of the AX solution.

The material removed by centrifugation was of a gelatinous nature. The presence of soft gelatinous material in the material retained during dead-end filtration increases the specific filter cake resistance due to its ability to deform and fill the voids in the filter cake [110], reducing the porosity of the filter cake. This gel could be composed of a number of gel-forming substances present in wheat bran, such as oxidative crosslinked feruloylated AX [111] or irreversibly gelled cellulose [112]. After repeated washing of the insoluble material with deionized water it was found that the total dry solids content of the washed gel was less than 4 wt% (unpublished data).

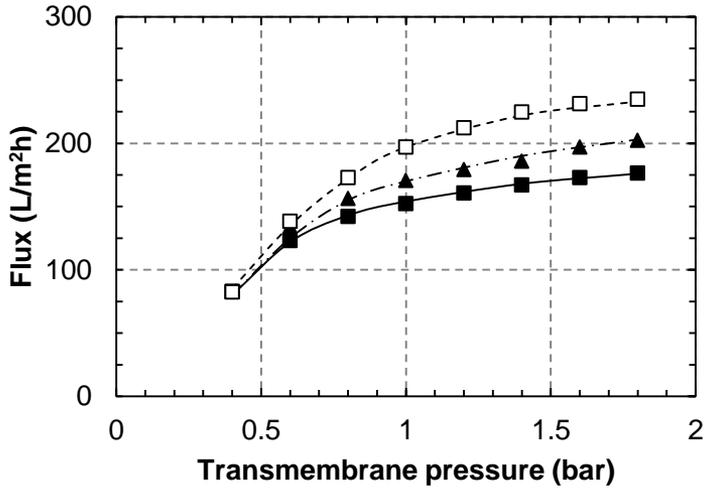
The effect of centrifugation on the subsequent dead-end filtration was also investigated (Paper I). Although the further removal of suspended material had only a limited effect on the UF flux, the effect on the filtration resistance was much greater, as can be seen in Figure 8. The time required to produce 50 L of

filtrate was reduced from 360 s with the untreated solution, to 180 s with the solution treated with a longer residence time in the nozzle separator, and to 110 s for the solution treated in the high-speed-centrifuge. The corresponding specific filter cake resistance was  $1.5 \cdot 10^{10}$  m/kg for the untreated solution and  $5.6 \cdot 10^9$  m/kg for the solution treated with a long residence time in the nozzle separator. The specific filter cake resistance of the solution treated with high-speed-centrifugation was even lower, but could not be quantified as the filtration pressure of 4 bar was not reached until the end of the filtration.



**Figure 8.** Filtration curves during dead-end filtration of untreated solution (■), the solution treated with a long residence time in the nozzle separator (▲) and the solution treated with high-speed-centrifugation (◻), using 2 wt% diatomaceous earth as filter aid. ( From Paper I)

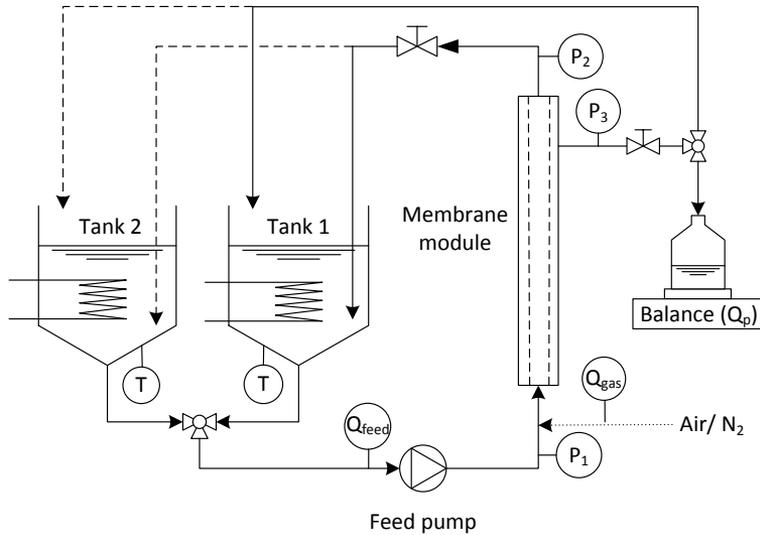
The turbidity and viscosity of the filtrate were lower when the solutions had been centrifuged for a longer time and at higher centrifugal forces before dead-end filtration. After dead-end filtration of the solution treated in the high-speed-centrifuge for 15 min at 30 000 g the turbidity and viscosity at 80 °C were reduced to 100 NTU and 0.9 mPa·s, respectively. UF of the dead-end-filtered solution showed that the dead-end filtration increased the UF flux, as reported previously [107]. Furthermore, increased centrifugation before dead-end filtration resulted in a higher UF flux, as can be seen in Figure 9.



**Figure 9.** Flux during UF at 80 °C and a CFV of 4 m/s of the untreated solution (■), the solution treated with a long residence time in the nozzle separator (▲) and the solution treated with high-speed-centrifugation (□). All solutions was pretreated by dead-end filtration before UF. (From Paper I)

## 6.3 Gas sparging

The impact of gas sparging during UF was also investigated. During these experiments the membrane filtration set-up was modified so that gas could be injected just before the membrane module. The recirculation loop was removed to avoid the accumulation of gas here, so that the set-up could be operated as an open-loop system. Additionally, the retentate outlet to the feed tank was lowered so that the outlet was well *below* the liquid surface, eliminating unintentional mixing of gas and liquid in the feed tank. The modified membrane set-up is shown in Figure 10.



**Figure 10.** Schematic of the membrane equipment used for the gas sparging experiments (Papers II-IV).

It was found that sparging dead-end-filtered solution during UF increased the flux (Paper viiiII). The highest increase in flux was obtained at high temperature and low CFV. It was estimated that gas sparging in an open-loop system would reduce the energy requirement for the initial stage of UF from  $5.3 \text{ kWh/m}^3$  permeate to  $2.6 \text{ kWh/m}^3$  at  $80^\circ\text{C}$  and a CFV of  $1 \text{ m/s}$ .

However, an open-loop system is not optimal from the perspective of energy demand, as the retentate is depressurized after every passage over the membrane, as the retentate is returned to the feed tank. The set-up originally used (Paper I, Figure 6) had a lower energy requirement as a recirculation loop was employed, and the recirculation pump only needs to compensate for the frictional pressure drop over the membrane module. The energy requirement of such a system operated continuously at a fixed VR will depend on the VR; a lower VR leading to an increased feed flow that will have to be pressurized. However, if the first stage in a multi-stage membrane plant were to be operated at a VR of 30%,  $80^\circ\text{C}$ , a CFV of  $7 \text{ m/s}$  and under limiting flux, the feed flow would constitute only 2.6% of the total volumetric flow over the membrane. The energy demand of the initial stage in such a plant was estimated by approximating the system to a dead-end batch filtration set-up, where the entire liquid retentate and air flow are recirculated in the recirculation loop. Using such a set-up would reduce the energy requirement compared to the open loop system. At a CFV of  $1 \text{ m/s}$  the energy requirement would be  $0.96 \text{ kWh/m}^3$  without air sparging and  $0.51 \text{ kWh/m}^3$  with air sparging. Increasing the CFV increases the energy requirement, such that at  $7 \text{ m/s}$  the energy requirement would be  $12.4 \text{ kWh/m}^3$  without air sparging and  $6.5 \text{ kWh/m}^3$  with air sparging. The benefit of using a higher CFV is that a higher

limiting flux is obtained and the membrane area required is smaller. The membrane area required to produce 1 m<sup>3</sup>/h permeate, at 80 °C with air sparging, decreases from 13.5 m<sup>2</sup> to 3.3m<sup>2</sup> when the CFV is increased from 1 m/s to 7 m/s.

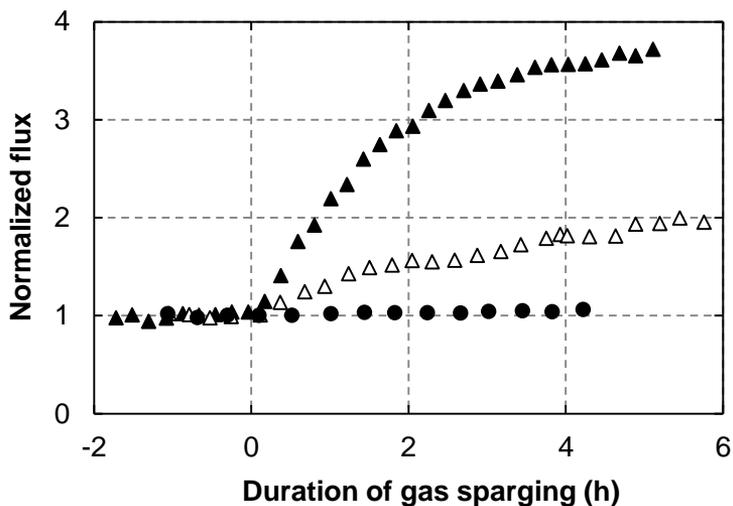
When using gas sparging as a flux-enhancing method during membrane filtration, the greatest increase in flux is usually obtained under conditions where fouling and concentration polarisation are more severe [113, 114]. In the study described in Paper II it was seen that when air sparging was used during UF of the hemicellulose solution, the benefit of gas sparging was greater when the CFV was low. This is in line with theory, as the concentration polarisation increases at lower CFV. However, the increase in flux was not as apparent when the temperature was decreased, and no flux increase was observed at 30 °C. These observations motivated further investigations on the mechanism of the flux enhancement during air sparging of the alkaline hemicellulose extract.

### **6.3.1 Role of oxygen during gas sparing**

Three new gas sparging experiments were conducted to further study the flux enhancement observed during air sparging at 80 °C (Paper III). Two batches of hemicellulose solution were pretreated by dead-end filtration, one of which was sparged with air during UF and the other with nitrogen. A batch of untreated hemicellulose solution was also sparged with air during UF to study the impact of dead-end filtration on the subsequent air sparging.

Each experiment started with UF without gas sparging to obtain a baseline flux, as shown in Figure 11. A sudden increase in flux is usually observed when gas sparging is used, which quickly stabilizes at the new higher level [88]. However, during these experiments, a gradual increase in flux was observed when sparging with air. The flux of the dead-end-filtered solution increased rapidly during the first 2 hours of air sparging, followed by a more modest rate of flux increase. After 4 hours of air sparging the flux of the dead-end-filtered solution had increased to 220 L/m<sup>2</sup>h, corresponding to an increase in flux by a factor of 3.5. The flux increase during air sparging of the untreated solution was more modest, increasing by a factor of 1.8 after 4 hours of air sparging.

No change in flux was observed during nitrogen sparging of the dead-end-filtered solution. This shows that the increase in flux is not due to a reduction in the concentration polarisation layer caused by the two-phase flow, but is rather caused by the mixing of oxygen in the alkaline solution.

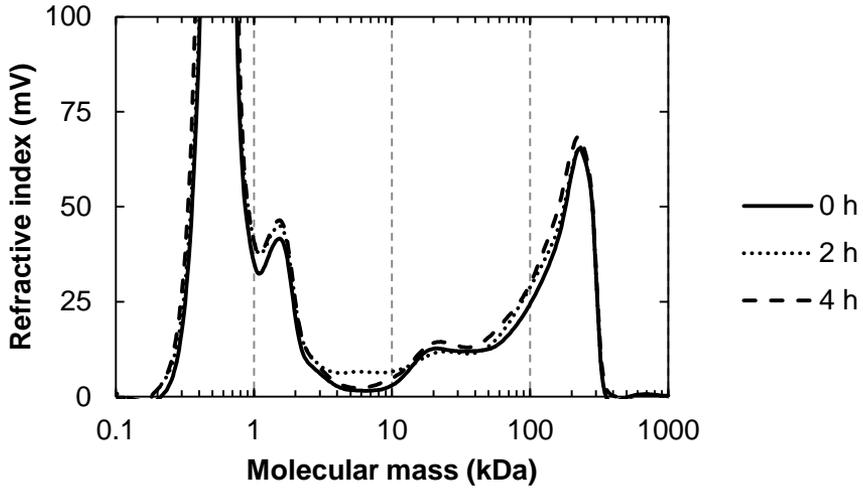


**Figure 11.** Flux enhancement factor during the gas sparging experiments using untreated solution with air sparging ( $\Delta$ ), dead-end-filtered solution with air sparging ( $\blacktriangle$ ), and dead-end-filtered solution with nitrogen sparging ( $\bullet$ ). (From Paper III)

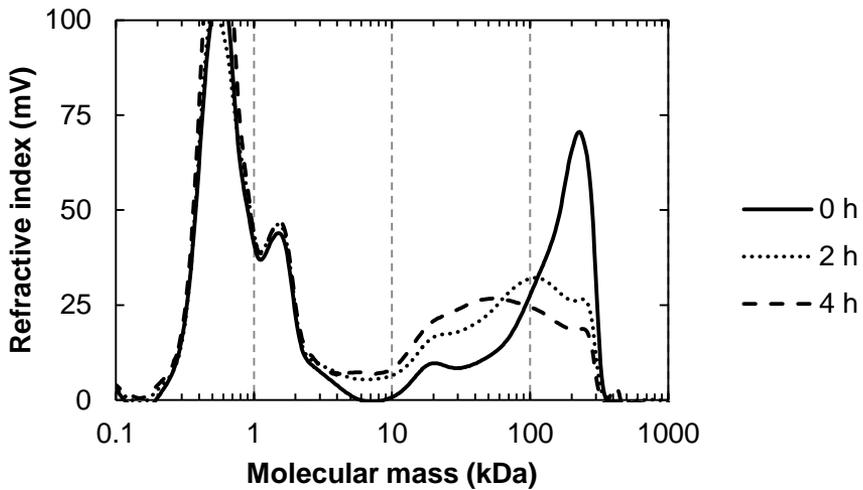
The molecular size distribution of the hemicelluloses in the nitrogen- and air-sparged dead-end filtered solutions are shown in Figure 12 and Figure 13, respectively. A decrease in solution viscosity, due to degradation of hemicelluloses during prolonged storage (72 h) at high temperature (80 °C), has been reported previously [115]. However, no degradation of the hemicelluloses was observed in the nitrogen-sparged solution, probably because of the relatively short time the solution was heated.

Severe degradation of the hemicelluloses was observed in the air-sparged solution. This further supports the hypothesis that the hemicelluloses are degraded when exposed to oxygen under alkaline conditions at high temperature. The mechanism causing degradation is thought to be a mild form of alkaline wet air oxidation, which is normally carried out at temperatures above 150 °C [116, 117] and used for pretreatment prior to enzymatic hydrolysis and fermentation. Holloway [118] also found that AX was partially degraded when wheat bran AX was delignified using sodium chlorite, resulting in a lower solution viscosity.

It is interesting to note that the hemicelluloses in the solution that had not been pretreated by dead-end filtration were degraded to a lesser extent by air sparging than the hemicelluloses in the dead-end-filtered solution. It has been reported that certain high-molecular-mass polysaccharides exhibit antioxidant activities [25, 119]. It is therefore possible that the suspended material removed during dead-end filtration has these properties, and thus protects the hemicelluloses from oxidative degradation.



**Figure 12.** Molecular size distribution of the components in dead-end-filtered solution sparged with nitrogen for 0, 2 and 4 hours. (From Paper III)

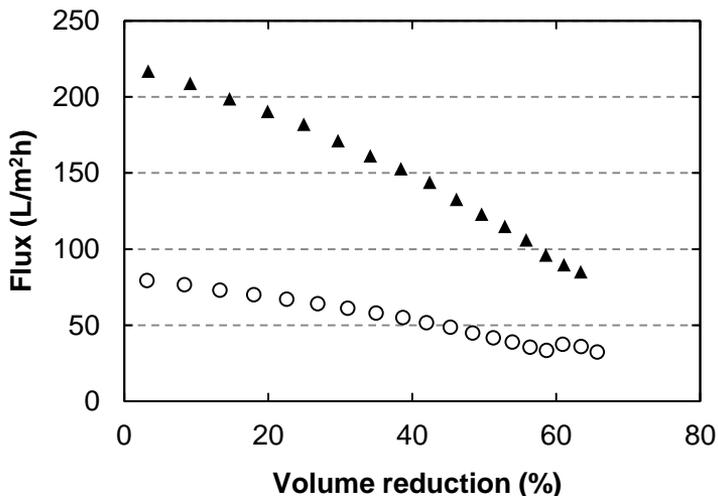


**Figure 13.** Molecular size distribution of the components in dead-end-filtered solution sparged with air for 0, 2 and 4 hours. (From Paper III)

## 6.4 Concentration and diafiltration

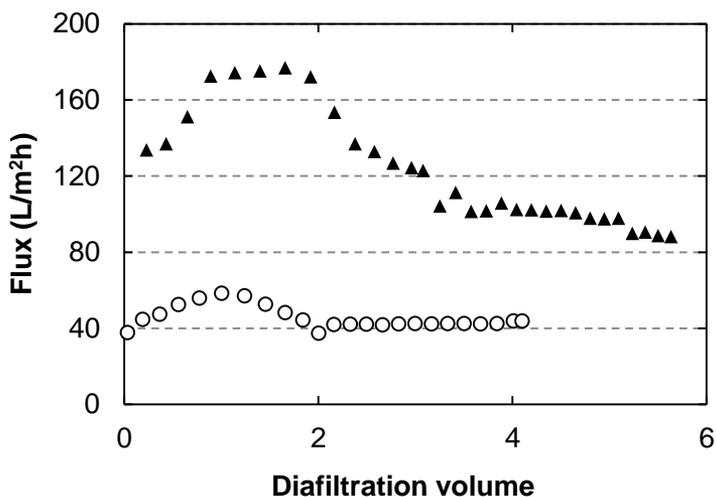
The economic impact of air sparging was studied by purifying two batches of dead-end filtered hemicellulose solutions with UF and DF (Paper IV). One of the batches was pretreated by air sparging for 4 h prior to UF. Both hemicellulose

solutions were then concentrated using UF to a VR of about 65%, and then subjected to DF until a permeate conductivity of 1 mS/cm was reached. It was found that air sparging of the hemicellulose solution increased the average flux during UF from 52 L/m<sup>2</sup>h to 151 L/m<sup>2</sup>h, as shown in Figure 14.



**Figure 14.** Flux during UF of air-sparged (▲) and non-sparged (○) dead-end-filtered hemicellulose solution (From Paper IV).

During DF the flux of both solutions increased initially, as solutes were washed out of the solution and the viscosity decreased. As DF progressed, the flux started to decline again, probably due to changes in the interactions between the AX molecules [107]. The average flux during DF increased from 46 L/m<sup>2</sup>h, to 130 L/m<sup>2</sup>h when the solution had been treated with air sparging before UF, as shown in Figure 15.



**Figure 15.** Flux during DF of air-sparged (▲) and non-sparged (○) dead-end-filtered hemicellulose solution (From Paper IV).

## 6.5 Cost estimates

The cost of concentration and purification of AX by UF and DF was estimated and is reported in Paper IV. A higher flux during UF and DF will result in a smaller membrane area being required to treat a specific volume of AX extract. However, it was seen that a higher DF volume was required for the air-sparged solution, and that the yield of hemicelluloses was lower. This will result in a higher cost of DF water, and a smaller amount of product will be produced from the same amount of raw material. The organic material not included in the product will have to be managed by other means. In this example, it was assumed that all the organic material not included in the product will end up in the waste water, and thus the cost of waste water treatment was included.

It can be seen from Table 3 that the cost of DF water and waste water treatment is indeed higher for the air-sparged solution. However, the benefit of higher flux resulting from air sparging lead to an overall decrease in the cost of purification, from 1128 €/ton hemicelluloses to 737 €/ton hemicelluloses.

**Table 3.** Capital and operating costs for the UF and DF of wheat bran hemicelluloses (Paper IV)

<b>Cost (€/ton hemicelluloses)</b>	<b>Non-sparged</b>	<b>Air-sparged</b>
<b>Capital cost</b>	330	179
<b>Operating costs</b>	798	557
- Electricity	307	166
- Membrane replacement	194	106
- Cleaning	25	13
- Maintenance and labour	165	90
- DF water	108	183
- Waste water treatment	244	386
<b>Total cost of membrane purification</b>	1128	737

## 6.6 Recovery of extraction chemicals

The UF permeate contains the chemicals used for the extraction of the hemicelluloses, and low-molecular-mass contaminants such as lignin. If the low-molecular-mass impurities can be removed, it would be possible to reuse the UF permeate for the extraction of more hemicelluloses. As the extraction chemical, NaOH, with a molecular mass of 40 Da, is considerably smaller than most of the impurities, which have molecular masses of  $\geq 400$  Da, it is possible to use NF to purify the UF permeate.

The molecular mass cut-off of the membrane is a trade-off between capacity and rejection, as membranes with a lower molecular mass cut-off usually also have lower permeability. Arkell et al. [74] showed that polymeric membranes with a molecular mass cut-off of 1 kDa showed very high rejections of both the contaminants lignin and sugars, and low rejection of NaOH. A cost estimate showed that due to the high cost of NaOH, investments in an NF NaOH recovery process would result in a very short pay-back time (2 months).

In addition to removing organic contaminants, NF will also remove large ions present in the solution, originating from the biomass. This was evident when the NF retentate was allowed to cool, as precipitation of inorganic salts was observed (unpublished data). The precipitate was filtered off, rinsed with deionized water and dissolved in 1% HNO<sub>3</sub>. The distributions of inorganic ions present in the liquid feed, retentate and precipitate are shown in Figure 16.

It can be seen that, while Na is the dominating element among the ions, larger ions were retained by the NF membrane, as expected. This shows that the NF treatment also can partially reduce the accumulation of these compounds in the process when the extraction chemicals are recovery and recycled.

Compared with the NF retentate, the precipitate was enriched in P and Ca. It is possible that the precipitate consists of a complex between Na, Ca and phytic acid, which is a P storage compound found in many plants.

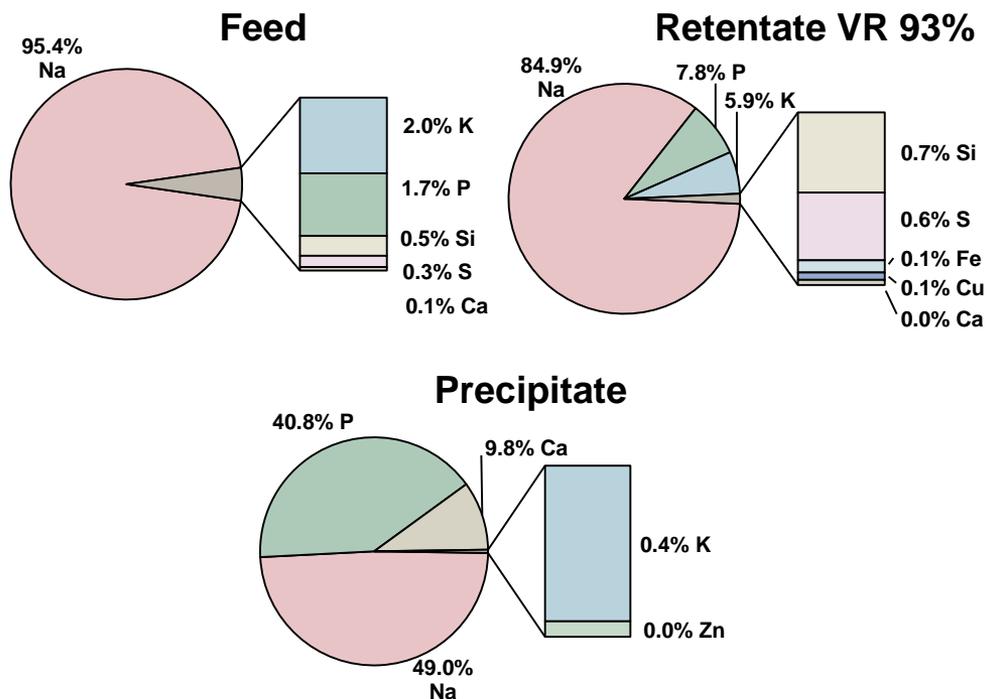


Figure 16. Composition of inorganic material in NF feed, NF retentate and from the precipitate in the NF retentate.

## 6.7 Final remarks on arabinoxylan recovery

The choice of purification method for the extracted AX depends on the desired properties of the intended product, such as the molecular mass and restrictions on particle content. If the molecular mass of the AX is higher than required, it can be reduced by air sparging, which will increase the UF and DF fluxes and decrease the production cost.

If particulate matter is acceptable in the product, the pretreatment of the crude AX extract by dead-end filtration with diatomaceous earth could be removed. This would simplify the process by removing a process step and reduce the cost, in terms of both reduced capital investments and elimination of the cost of diatomaceous earth.

If a particle free-product is required, centrifugation of the solution will be an important means to reduce the filtration resistance of the solution, thus reducing the amount of filter aid required. The possibility of filter aid recovery and recycling should also be considered if it is anticipated that large amounts of filter aid will be needed.

## 7. Spruce Galactoglucomannan

Numerous organic components dissolve during the pulping of wood and end up as solutes in the pulp suspension. Some of these components cause problems during the paper-making process [120]. In addition, some of the compounds are anionic and will react with, and increase the demand for, cationic retention aids, which is why these components are sometimes referred to as “anionic trash”. In order to restrict the concentration of these components many paper mills bleed them out of the process. This leads to a high consumption of fresh water; for TMP about 10-30 m<sup>3</sup>/air dried ton pulp [121].

In 1994, Thornton et al. [18] showed that the polysaccharide *O*-acetyl-galactoglucomannan was the main wood component dissolved in the process water during thermomechanical pulping of spruce. The amount of GGM released corresponded to 10% of the total amount of GGM in spruce wood, which is about 1.6% of the total wood mass. A process for the recovery and fractionation of dissolved substances from the process water from TMP mills was patented a few years afterwards [122]. In this process, adsorption was employed for the recovery of aromatic material, and UF for the recovery of the dissolved GGM [123]. This process was later scaled up to produce GGM on the kg-scale [4]. Another proposed process configuration is the use of MF-UF-NF to sequentially fractionate the components in the TMP process water based on their size [70, 124].

In the present work, the recovery of spruce GGM using membrane filtration was further studied, focusing on the scaling-up of the process. The impact of MF membrane pore size on UF performance was investigated (Paper V), and the composition of the substances responsible for the persistent fouling of the UF membrane was studied (Paper VI).

A pilot trial on the recovery of GGM using MF and UF was carried out at a TMP mill to investigate the performance of continuous MF and UF (Paper VII). The cost of the process was estimated based on the results of the pilot trial and laboratory experiments.

Finally, the possibility of increasing the molecular mass of the isolated GGM using laccase-catalysed linkage of aromatic moieties was investigated (Paper VIII).

## 7.1 Thermomechanical pulp mill process water

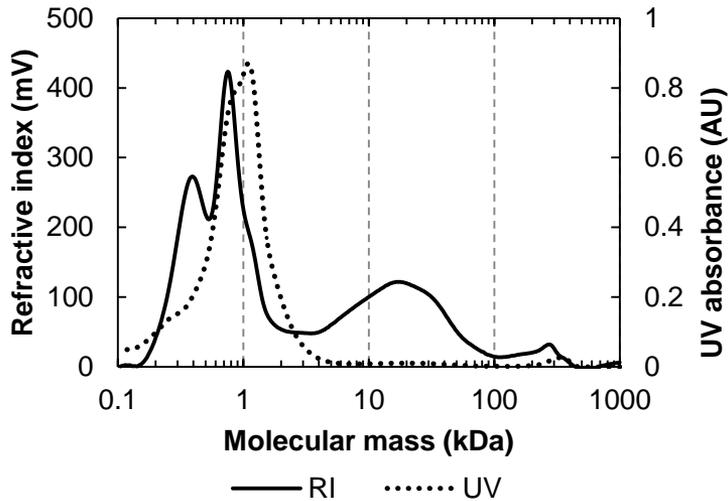
The source of spruce GGM in this work was process water from a TMP mill. The TMP mill process water was withdrawn after a disc filter, which separates the refined pulp from the process water. Typical concentrations of solutes are given in Table 4. As can be seen, the TMP mill process water is relatively dilute, containing less than 1 wt% total solids. Apart from GGM, the TMP mill process water contains residues of fibres, lignin, salts and extractives, both dissolved and in colloids stabilized by adsorbed polysaccharides [125].

**Table 4.** Typical composition of thermomechanical pulp mill process water (Paper VI)

<b>Total solids (g/L)</b>	6.7
<b>Ash (g/L)</b>	1
<b>Hemicelluloses (g/L)</b>	2
- Arabinan (g/L)	0.1
- Galactan (g/L)	0.3
- Glucan (g/L)	0.4
- Mannan (g/L)	1.2
<b>Total lignin (g/L)</b>	0.8
<b>Turbidity (NTU)</b>	604

A typical molecular mass distribution of the components present in the TMP mill process water is shown in Figure 17. As can be seen from the UV response, most of the aromatic components in the TMP process water have low molecular mass, about 1 kDa. The colloidal extractives are also seen as a small peak of high-molecular-mass components in the RI and UV chromatograms.

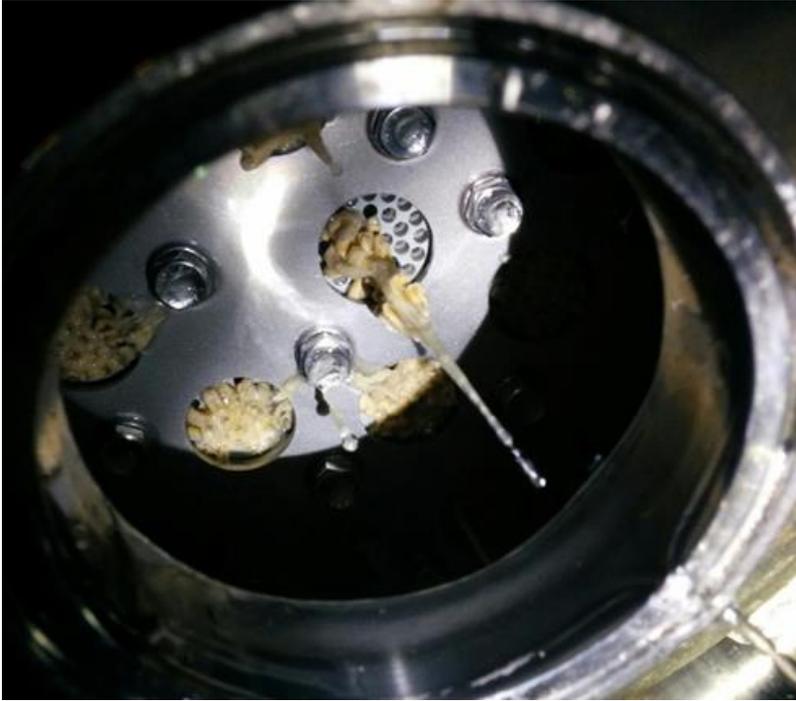
From the RI curve it can be seen that the TMP mill process water contained a large amount of material of about 15 kDa, consisting of polysaccharides as shown in lack of signal from the UV detector. Salts, acids, mono- and oligosaccharides and the low molecular mass lignin are seen as peaks in the low-molecular-mass region of the RI chromatogram. Krawczyk and Jönsson [71] fractionated the components in TMP process water using SEC, and reported that the high-molecular-mass polysaccharides consisted almost exclusively of GGM, while polysaccharides consisting of arabinose, galactose and glucose subunits were found among the low-molecular-mass fractions.



**Figure 17.** Molecular mass distribution of components in the TMP mill process water (unpublished data) analysed using SEC, with the same method as described in Paper V. Note that PEG, with molecular weights of 0.4-35 kDa was used as standards, and the sizes of molecules > 35 kDa are extrapolated and thus do not represent the true molecular mass.

## 7.2 Prefiltration

Pulp mill process water usually contains residual pulp fibres. Even filtrates after drum/disc filters can contain a considerable amount of fibres due to damaged filter cloths leading to incomplete retention of fibres. These fibres can cause problems in process equipment during membrane filtration, especially blocking of flow channels, as shown in Figure 18. One method of reducing this problem is to use channels with large diameters. However, this will increase the footprint and cost of the membrane plant. Another way of counteracting this problem is to add an additional prefiltration step before the membrane unit to remove the residual wood fibres. Different types of filters can be used to remove fibres. Persson et al. [124] used a rotary drum filter and during the pilot trial presented in Paper VII an automatic self-cleaning basket filter was used.



**Figure 18.** Inlet of MF membrane elements, plugged by fibres. (Photo from the pilot trial presented in Paper VII).

It is important to consider the shape of the fibres when deciding which type of filter should be used. During the pilot trial presented in Paper VII, it was found that a filter with circular 100  $\mu\text{m}$  holes retained fibres considerably better than a filter with 40  $\mu\text{m}$  wide slots. This is because the fibres can become oriented such that they can pass through the slots, despite the fact that they are much longer than the width of the slots. If the filter has circular holes, only a few fibres will pass through the filter “head first” provided the holes are larger than the width of the fibre.

### 7.3 Microfiltration

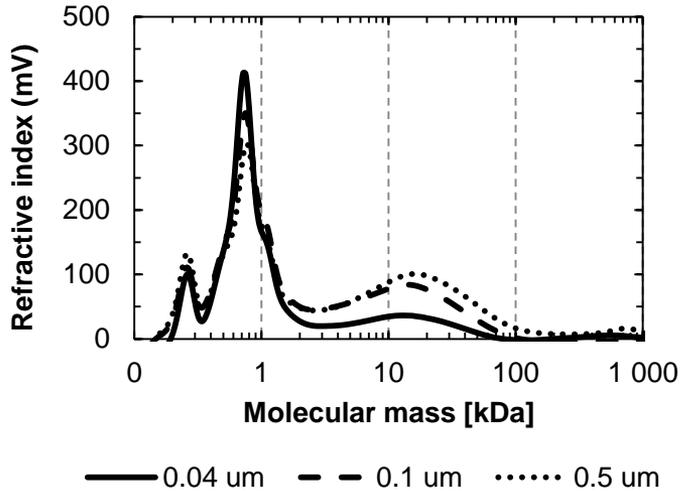
The prefiltered process water contains suspended material such as colloidal extractives and fibre fragments [124]. These components can be detrimental to product properties and must be removed before the GGM is recovered using UF. Furthermore, wood extractives can cause allergic reactions [126]. Removing the colloidal material will also improve the downstream UF performance (Papers V and VI).

Krawczyk and Jönsson [71] showed that, although only about 10% of the particles in prefiltered TMP mill process water were smaller than 1  $\mu\text{m}$ , they could cause considerable problems during MF when the MF membrane pore size was close to 1  $\mu\text{m}$ . However, they also found that the retention of GGM during MF was reduced when using a MF membrane with larger pores, thus increasing the yield of GGM recovered in the MF permeate.

### **7.3.1 Influence of MF on UF performance**

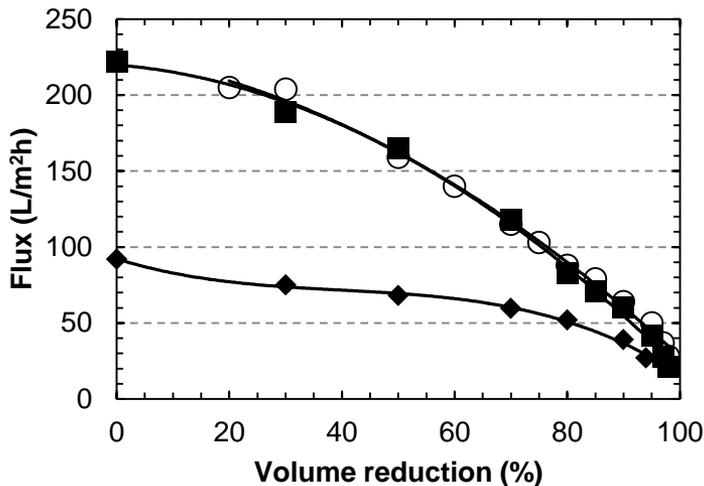
The possible benefit in terms of increased GGM yield must be considered in relation to possible effects on downstream processing. The impact of MF membrane pore size on UF was thus further studied (Paper V). Previous studies using hot water prehydrolysate have shown that the removal of large contaminants using a more open membrane before the recovery of hemicelluloses resulted in a higher UF flux and reduced membrane fouling [127].

To investigate the impact of small colloids present in the MF permeate during GGM recovery from TMP mill process water, the process water was filtered using MF membranes with different pore sizes. It was found that with increasing MF membrane pore size, the turbidity of the MF permeate increased as the retention of the extractives decreased; a large difference in turbidity being seen between the permeates produced with MF membranes with pore sizes of 0.1  $\mu\text{m}$  and 0.5  $\mu\text{m}$  (14 versus 105 NTU). This is in agreement with reports on the size of the colloids, 0.2-2  $\mu\text{m}$  [128]. The lower retention of hemicelluloses with MF membranes with larger pore sizes was observed in the present work as a higher content of high-molecular-mass hemicelluloses in the MF permeate, as shown in Figure 19.



**Figure 19.** Molecular mass distribution of components in MF permeate using a membrane with a pore size of 0.04  $\mu\text{m}$  (solid line), 0.1  $\mu\text{m}$  (broken like) and 0.5  $\mu\text{m}$  (dotted line). (From Paper V)

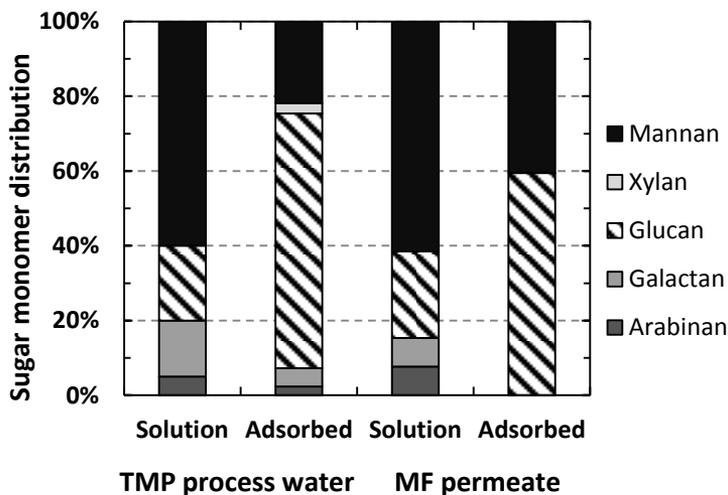
The higher content of colloidal material in the MF permeate using the 0.5  $\mu\text{m}$  pore membrane was reflected in a drastically lower UF flux, as can be seen in Figure 20. However, as the content of high-molecular-mass GGM was higher, the GGM yield during UF increased with increased MF membrane pore size, from 70% to 90% using the 0.04  $\mu\text{m}$  and 0.5  $\mu\text{m}$  membranes, respectively.



**Figure 20.** Flux during UF of MF permeates produced using MF membranes with different pore sizes. The pore sizes of the MF membranes were 0.04  $\mu\text{m}$  ( $\circ$ ), 0.1  $\mu\text{m}$  ( $\blacksquare$ ) and 0.5  $\mu\text{m}$  ( $\blacklozenge$ ). The temperature during UF was 60  $^{\circ}\text{C}$ , the transmembrane pressure 4 bar and the cross-flow 1.3  $\text{m}^3/\text{h}$ . (From Paper V)

The colloidal material not only causes a decrease in UF flux, but it also adheres to the membrane, causing fouling. The process water is known to contain numerous solutes that are prone to cause membrane fouling. Known foulants include not only colloidal and dissolved extractives [95, 96], but also polysaccharides [97]. It was shown that residues of deposited polysaccharides remained on the membrane surface even after repeated chemically enhanced cleaning (Paper VI). The amount of polysaccharides remaining on the membrane surface was considerably higher when filtering TMP mill process water than when filtering the MF permeate: 508 mg/m<sup>2</sup> versus 37 mg/m<sup>2</sup>, respectively.

The polysaccharides adsorbed onto the membrane surface contained a high amount of glucan, as can be seen in Figure 21. GGM, which is the dominating polysaccharide in the TMP mill process water, has a glucan: mannan ratio of 1:3, while the ratios for the polysaccharides deposited on the membranes treating TMP mill process water and MF permeate, were 1:0.3 and 1:0.7, respectively. This shows the presence of polysaccharides with a high glucan content, possibly  $\beta$ -glucan or starch, present in the feed solution at low concentration are responsible for a large part of the membrane fouling.

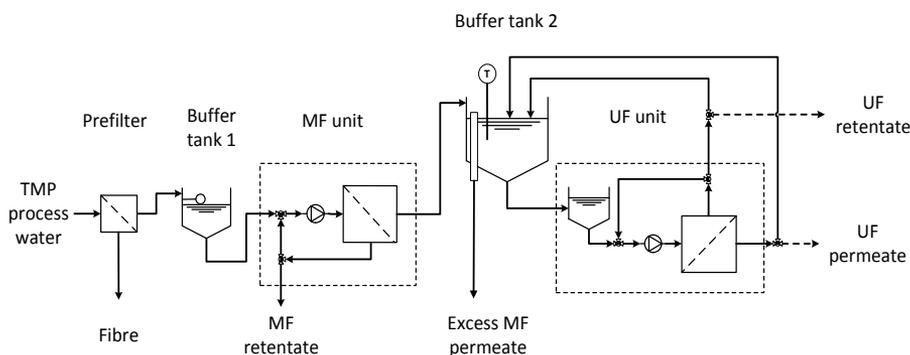


**Figure 21.** Distribution of monosaccharide subunits in the feed solutions and material adsorbed on the membrane remaining after cleaning.

## 7.4 On-site pilot trial

A schematic of the pilot plant used in the on-site pilot trial is shown in Figure 22. The prefilter was a Heco Hiflux Auto-Line M, equipped with a filter basket of 860 cm<sup>2</sup> with perforated 100 µm circular holes, equipped with a scraper capable of cutting fibres stuck in the holes. The MF unit consisted of a Liqtech MultiBrain pilot unit equipped with 26 ceramic tubular Liqtech UF membranes, giving a total membrane area of 8.6 m<sup>2</sup>. The MF membranes were made of SiC, with an inner channel diameter of 3 mm, and a pore size that gives it characteristics that of the boundary between UF and MF.

The UF unit was an Alfa Laval 70236-6.3" MF/UF pilot plant. The UF unit could be equipped with between one and nine 6.3" spiral wound elements, each with a membrane area of 15.75 m<sup>2</sup>. The spiral wound elements were equipped with 48 mil spacers.



**Figure 22.** Schematics of the pilot plant used for the recovery of hemicelluloses using MF and UF. (Paper VII)

The pilot unit processed 1.6 m<sup>3</sup>/h of TMP mill process water, when MF was operated at a VR of 50%, thus delivering 0.8 m<sup>3</sup>/h MF permeate to the UF unit. The UF permeate and retentate were recirculated to Buffer tank 2 when the feed consumption of the UF unit was higher than the MF permeate volume delivered by the MF unit (e.g. at a UF flux >50 L/m<sup>2</sup>h at a VR of 98%, when a single spiral wound UF element was used).

### 7.4.1 Microfiltration

The transmembrane pressure of the MF unit was maintained at about 0.3 bar. During constant flux operation, the pressure increased over time. However, this was mainly due to the accumulation of fibres in the inlet of the MF membranes, causing plugging of the flow channels (as shown in Figure 18). After fibre

removal, which was on May 15 and on May 18, the transmembrane pressure was reduced again, as shown in Figure 23. After the manual removal of fibres the frictional pressure drop decreased from 0.7 bar to 0.5 bar. The high frictional pressure drop in relation to the low transmembrane pressure probably resulted in a negative transmembrane pressure at the end of the membrane module, causing MF permeate loss. A slight increase in the retention of hemicelluloses was also noted over the time period of Figure 23, due to the slight build-up of membrane fouling.

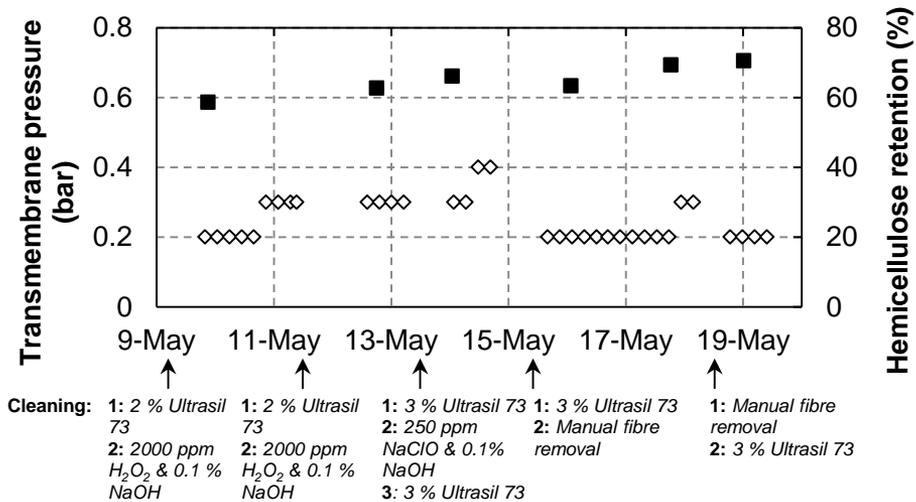
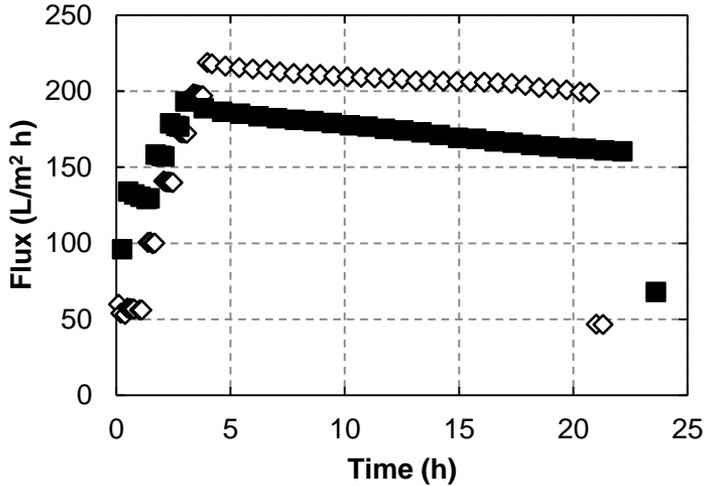


Figure 23. Observed transmembrane pressure (◊) and hemicellulose retention (■) during 10 days of the MF pilot trial at the pulp mill.

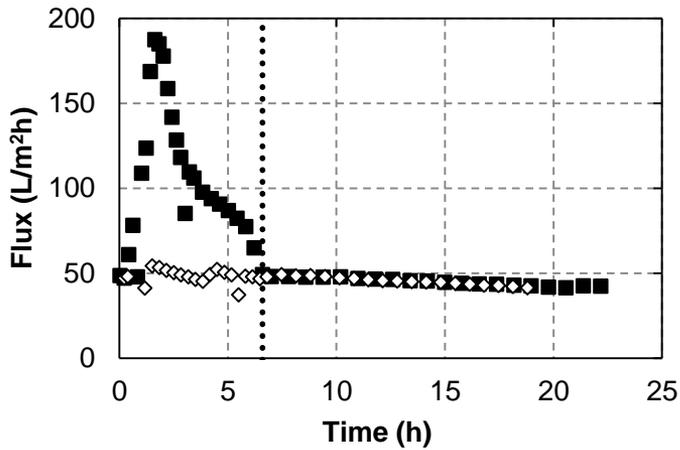
## 7.4.2 Ultrafiltration

The performance of continuous UF at different VRs was investigated using a single RC10 PE spiral wound element from Alfa Laval. The average flux at a transmembrane pressure of 5.95 bar was 210 L/m<sup>2</sup>h, during 17 hours at a VR of 50%, and 178 L/m<sup>2</sup>h during 20 hours at a VR of 80%, as shown in Figure 24. The retention of hemicelluloses was 88% and 93.5% at the VR of 50% and the VR of 80 %, respectively.



**Figure 24.** Flux during UF at constant VR; 50% (◇) and 80% (■). The temperature was 60 °C and the frictional pressure drop over the element was 1.1 bar. (From Paper VII)

When the performance was studied at a VR of 98% the pilot unit was initially operated in dead-end filtration mode to increase the concentration of GGM in the recirculation loop. As the capacity of the UF plant exceeded the rate of production of MF permeate unless it was operated at high VR, two methods were used to achieve the concentration corresponding to a VR of 98% before the UF retentate was collected. The first method was to first increase the transmembrane pressure to 5.95 bar, and discard the UF permeate. As can be seen in Figure 25, this led to an initial flux of 185 L/m<sup>2</sup> h, which then quickly decreased as the concentration in the recirculation loop increased. After running the experiment for 3 hours the MF permeate in the buffer tank before the UF unit had been consumed, and UF permeate had to be recycled to the internal feed tank for a period of 1.5 hours before sufficient MF permeate had been produced to continue UF concentration. When the concentration in the recirculation loop corresponded to a VR of 98%, the flux had decreased to 68 L/m<sup>2</sup>h. The transmembrane pressure was then reduced to 2.45 bar, yielding a flux of 50 L/m<sup>2</sup>h, matching the production of MF permeate, and the collection of UF retentate began.



**Figure 25.** Flux over time during UF at a VR of 98% conducted on May 17(■) and May 18 (◇). The VR was increased to VR 98% the first 7h, and maintained at this level thereafter. The transmembrane pressure was increased directly to 5.95 bar on May 17, while the flux was maintained at 50 L/m<sup>2</sup>h by increasing the transmembrane pressure stepwise to 5.95 bar on May 18.

The second method used was to gradually increase the transmembrane pressure while maintaining a flux of 50 L/m<sup>2</sup>h. Both methods resulted in the same flux at the same VR and transmembrane pressure, which decreased to 43 L/m<sup>2</sup>h after 11 hours at constant pressure. The retention of hemicelluloses at a VR of 98% was 98%, and the concentration of hemicelluloses in the UF retentate was 30 g/L.

### 7.4.3 Cost estimate

The cost of the membrane processes used for producing GGM from TMP mill process water was estimated. The cost of pretreatment was not included in this work. However, Persson et al. [70] estimated that pretreatment using drum filtration would cost 40 €/ton GGM produced. Neither has the product formulation been considered in this work, as it is highly product-specific.

The cost of GGM recovery by membrane filtration was estimated based on the experimental data obtained from lab-scale experiments and the on-site pilot trial ( Paper VII). A brief breakdown of the costs is presented in Table 5.

The estimated cost of 1160 €/ ton GGM produced is higher than earlier estimates [129]. This is because it was not possible to maintain the high flux obtained previously during MF during batch concentration studies when MF was operated in continuous mode.

**Table 5.** Costs of microfiltration and ultrafiltration in GGM recovery from TMP mill process water. (From Paper VII)

	<b>Microfiltration</b>	<b>Ultrafiltration</b>
<b>Capital [€/t<sub>hemi</sub>]</b>	<b>390</b>	<b>56</b>
<b>Operating cost [€/t<sub>hemi</sub>]</b>	<b>463</b>	<b>250</b>
- Electricity [€/t <sub>hemi</sub> ]	61	26
- Membrane exchange [€/t <sub>hemi</sub> ]	100	59
- Cleaning [€/t <sub>hemi</sub> ]	108	138
- Maintenance and labour [€/t <sub>hemi</sub> ]	195	28
<b>Total [€/t<sub>hemi</sub>]</b>	<b>853</b>	<b>306</b>
<b>Total cost [€/t<sub>hemi</sub>]</b>	<b>1159</b>	

The concentration of GGM in the UF retentate produced during the on-site pilot trial was 30 g/L, while it was estimated to be 46 g/L in the cost estimate. This is because the MF during the on-site trial was operated at a VR of only 50%. In the cost estimate it was assumed that the VR during MF would be higher, which would lead to a higher initial concentration of GGM during UF, resulting in a higher final concentration.

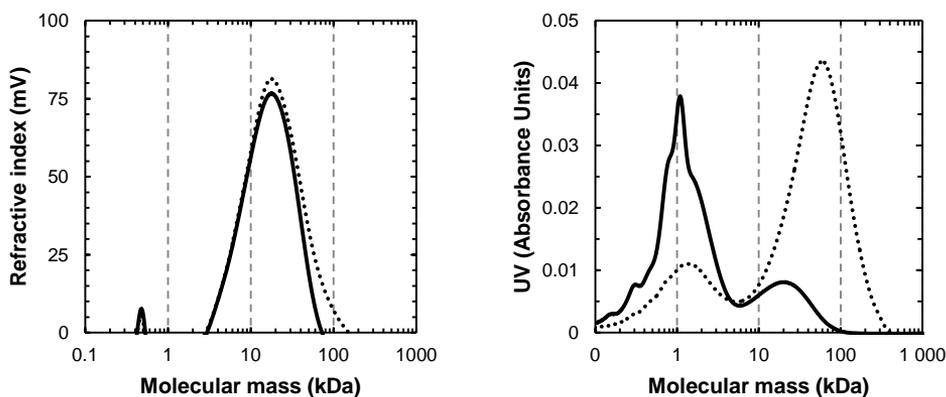
Further concentration of the GGM and possibly drying of the product will be needed depending on the product requirement. Additional UF concentration can be conducted using a plate-and-frame set-up. Other alternatives include the formulation of the GGM into a powder by antisolvent precipitation or spray drying [130].

## 7.5 Impact of enzymatic lignin polymerization

Low-molecular-mass lignin will pass through the UF membrane during GGM recovery. However, the yield of recovered organic polymers can be increased by polymerization of this lignin (Paper VIII). The low-molecular-mass lignin can be polymerized by laccase-mediated oxidation and coupling of lignin residues. Laccase is an enzyme used by fungi, bacteria and plants to catalyse the oxidation of a wide variety of compounds using oxygen [131], where one function is to facilitate the polymerization of lignin [132]. This property has been exploited to increase the molecular mass of hemicelluloses by taking hemicelluloses with aromatic side groups, and using laccase to catalyse the formation of bonds between the aromatic side groups, resulting in the covalent binding of two hemicellulose molecules through a bridge of the aromatic side groups [133, 134].

As it was observed that the UF retentate from the TMP process water exhibited some UV response at high molecular mass, the possibility of increasing the

molecular mass of the GGM using laccase was investigated in a study where the enzyme laccase was added to UF retentate (Paper VIII). The molecular size distribution before and after the enzymatic treatment is shown in Figure 26. The UV response, which is sensitive to aromatic compounds such as lignin, shows that most of the low-molecular-mass aromatics (~1 kDa) present in the TMP mill process water were polymerized into high-molecular-mass compounds by laccase. However, the RI response, which gives the size distribution of all the dissolved material, was almost unchanged. The small increase in the molecular size seen in the RI response is probably due to the added high-molecular-mass lignin molecules in the enzyme treated solution. The reason why polymerization of the lignin did not affect the RI response more is that the concentration of hemicelluloses in the solution was over 10 times higher than the concentration of lignin.



**Figure 26.** Molecular mass distribution of hemicelluloses (left) and lignin (right) (measured as UV absorbance at 280 nm) before (—) and after (····) enzymatic treatment with laccase. (From Paper VIII)

The high-molecular-mass material obtained after laccase treatment was then further purified by DF (Paper VIII). Salts were removed while no further increase was achieved in the hemicellulose/lignin ratio due to the increased molecular mass of the hemicelluloses. The increased molecular mass of the lignin resulted in a lignin retention of 87%, which is considerably higher than during the previous UF study (Paper V), where the final retention of lignin was 50%.

The permeate from DF was further treated with nanofiltration (NF). The NF membrane used was a spiral wound NF99HF membrane from Alfa Laval with a  $\text{MgSO}_4$  rejection of  $\geq 98\%$ . Using NF, it was possible to achieve 98% retention of the residual hemicelluloses and lignin components, yielding purified water with a total dry solids content of 0.25 g/L as permeate. NF can thus be used as a polishing step to remove dissolved components from the permeates of previous membrane filtration steps before the water is recirculated to the mill.

## 7.6 Final remarks on galactoglucomannan recovery

The dissolved high-molecular-mass polymers found in TMP mill process water can be recovered by MF followed by UF. The native high-molecular-mass polymers consisted mainly of GGM. Additional high-molecular-mass material can be recovered by laccase-catalysed polymerization of the aromatic low-molecular-mass material, and subsequent recovery by UF. This can be done to make the low-molecular-mass aromatic compounds easier to remove from the process water, reducing the chemical oxygen demand [135], or to increase the amount of polymeric material that can be obtained from TMP mill process water.

Increasing the MF flux would have the greatest improvement on the process economics. The channel diameter of the MF membranes used in this work was 3 mm. Larger channel diameters could be considered to reduce the frictional pressure drop and increase the Reynolds number, both of which have the potential to increase the MF flux. However, increasing the channel diameter will usually reduce the membrane area per membrane element, thus increasing the  $m^2$  cost even further for the MF membranes.

The highest cost in UF was membrane cleaning. However, this could potentially be reduced. It is possible that the volume of cleaning solution / $m^2$  membrane area could be reduced in a larger installation, reducing the consumption of cleaning chemicals. Furthermore, possible reuse of cleaning solution can be considered [136].

The recovery of GGM from TMP process water will also affect the rest of the mill. One of the main effects will be a reduction in the amount of organic matter that has to be treated in the waste water treatment plant. The cost of waste water purification varies depending on the treatment method and the contaminants to be removed. Assuming that the cost of purification is 0.28 €/kg organics removed [137], a saving of 280 €/ton pure GGM recovered could be made. This is without considering the concentrated stream of extractives, fines and other organics obtained as a MF retentate. The option of further concentration of the MF retentate, either by further membrane filtration and/or evaporation, before disposal of the MF retentate by incineration, should be considered.

## 8. Conclusions and Future Work

In this work, hemicelluloses extracted from wheat bran and spruce were recovered and purified using membrane filtration. For the purification process to be economical the membrane process must exhibit high filtration capacity, good selectivity and stable process operation. It was shown how different pretreatment methods could be used to obtain a higher and more stable flux, and cost estimates were made to highlight the impact of the different stages of the process on the total cost.

The hemicelluloses produced during these experiments will now be used to investigate different product applications. Improved knowledge on the properties of hemicelluloses and their cost of production will increase the probability of identifying applications with good economic potential. Once economically viable product applications have been found, the demand for these hemicelluloses will increase, which will further drive the commercialization of the processes required to recover them.

### 8.1 Arabinoxylan from wheat bran

The flux during UF of the high viscosity wheat bran extract could be drastically increased by sparging air through the solution, resulting in a considerably reduced purification cost. Sparging the solution with air reduced the molecular mass of the AX, reducing the viscosity of the solution and thus the cost of AX purification.

The solution of alkaline-extracted AX contained suspended material which resulted in high filtration resistance during pretreatment by dead-end filtration. After further investigations on the composition of the insoluble gel, it may be possible to develop a modified extraction method in which the amount of suspended gel in the alkaline AX solution is reduced or even eliminated. This would reduce the filtration resistance during dead-end filtration, reducing the amount of filter aid required.

Finally, it was shown that the cost of DF water was rather high during the purification of AX by UF and DF. The possibility of reducing the DF factor and using antisolvent precipitation as a final purification step should be considered.

Antisolvent precipitation removes water, hydrophobic impurities, and some salts from the product.

## 8.2 Galactoglucomannan from spruce

GGM was successfully recovered in an on-site pilot unit operated in continuous concentration mode. The concentration of hemicelluloses in the TMP mill process water was about 2 g/L and when the VR of the MF and UF units was 50% and 98%, respectively, an UF retentate containing 30 g hemicelluloses/L was obtained. However, a higher concentration of hemicelluloses could be obtained in the UF retentate when MF is operated at a higher VR.

The cost of the membrane processes used for the production of hemicelluloses from TMP mill process water was about 1160 €/ton; the greatest cost being that associated with the MF unit. Increasing the MF flux would thus have a considerable impact on the cost of the process. Possible MF flux-enhancing methods include back-pulsing [71] or using MF membranes with wider flow channels. The use of wider flow channels would reduce the risk of channel blockage by fibres, and may reduce cake formation at the membrane surface through the higher Reynolds number. Wider flow channels would also reduce the frictional pressure drop over the membrane element, reducing the risk of permeate losses due to local negative transmembrane pressures at the end of the elements. An additional method of reducing MF permeate losses due to negative transmembrane pressure at the end of the membrane module, other than using shorter membrane elements, is to prevent reversed permeate flow by partially filling the membrane module with gas [138].

A large contribution to the cost of UF arises from membrane cleaning. Optimization of the volume of cleaning solution used could reduce the cost of UF. It was shown in laboratory studies that some of the foulants that were difficult to remove from the UF membrane consisted of polysaccharides with high glucan content. Future optimization of the cleaning procedure, as well as new cleaning agents designed to target the foulants may reduce the cost of cleaning further.

During these studies, attention was directed to the recovery of GGM from TMP mill process water. The MF retentate obtained, consisting of concentrated extractives, fibre fragments and adsorbed hemicelluloses, was regarded as waste. Further studies on the recovery of extractives from the MF retentate could open up the possibility of obtaining products other than GGM from this process.

The low-molecular-mass aromatics in the UF permeate could potentially be recovered using adsorption, or polymerized into additional high molecular mass polymers and recovered using UF.



# References

1. McKendry, P., *Energy production from biomass (part 1): overview of biomass*. *Bioresour. Technol.*, 2002. **83**(1): p. 37-46.
2. Karimi, K., Shafiei, M., and Kumar, R., *Progress in Physical and Chemical Pretreatment of Lignocellulosic Biomass*, in *Biofuel Technologies: Recent Developments*, V.K. Gupta and M.G. Tuohy, Editors. 2013, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 53-96.
3. Naidu, D.S., Hlangothi, S.P., and John, M.J., *Bio-based products from xylan: A review*. *Carbohydr. Polym.*, 2018. **179**: p. 28-41.
4. Willför, S., Sundberg, K., Tenkanen, M., and Holmbom, B., *Spruce-derived mannans - A potential raw material for hydrocolloids and novel advanced natural materials*. *Carbohydr. Polym.*, 2008. **72**(2): p. 197-210.
5. Mikkonen, K.S. and Tenkanen, M., *Sustainable food-packaging materials based on future biorefinery products: Xylans and mannans*. *Trends Food Sci. Technol.*, 2012. **28**(2): p. 90-102.
6. Härdelin, L., Ström, A., Di Maio, E., Iannace, S., and Larsson, A., *Microcellular foaming of arabinoxylan and PEGylated arabinoxylan with supercritical CO<sub>2</sub>*. *Carbohydr. Polym.*, 2018. **181**: p. 442-449.
7. Konkol, Y., Vuorikoski, H., Tuomela, J., Holmbom, B., and Bernoulli, J., *Galactoglucomannan-rich hemicellulose extract from Norway spruce (*Picea abies*) exerts beneficial effects on chronic prostatic inflammation and lower urinary tract symptoms in vivo*. *Int. J. Biol. Macromol.*, 2017. **101**: p. 222-229.
8. Polari, L., Ojansivu, P., Mäkelä, S., Eckerman, C., Holmbom, B., and Salminen, S., *Galactoglucomannan extracted from Spruce (*Picea abies*) as a carbohydrate source for probiotic bacteria*. *J. Agric. Food Chem.*, 2012. **60**(44): p. 11037–11043.
9. Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Frederick Jr., W.J., Hallett, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.R., Murphy, R., Templer, R., and Tschaplinski, T., *The Path Forward for Biofuels and Biomaterials*. *Science*, 2006. **311**: p. 484-489.
10. Huang, H.-J. and Ramaswamy, S., *Overview of Biomass Conversion Processes and Separation and Purification Technologies in Biorefineries*, in

- Separation and Purification Technologies in Biorefineries*. 2013, John Wiley & Sons, Ltd. p. 1-36.
11. Nilsson, P. and Cory, N., *Skogsdata 2017*. 2017, Official Statistics of Sweden.
  12. Ländell, G., *Skörd av spannmål, trindsäd, oljeväxter, potatis och slåttervall 2016*. 2017, Statens Jordbruksverk.
  13. Kim, T.H., *Pretreatment of Lignocellulosic Biomass*, in *Bioprocessing Technologies in Biorefinery for Sustainable Production of Fuels, Chemicals, and Polymers*. 2013, John Wiley & Sons, Inc. p. 91-110.
  14. Phitsuwan, P., Sakka, K., and Ratanakhanokchai, K., *Improvement of lignocellulosic biomass in planta: A review of feedstocks, biomass recalcitrance, and strategic manipulation of ideal plants designed for ethanol production and processability*. *Biomass Bioenergy*, 2013. **58**: p. 390-405.
  15. Sjöström, E., *Wood Chemistry*. 2 ed. 1993, San Diego: Academic Press.
  16. Timell, T.E., *Recent progress in the chemistry of wood hemicelluloses*. *Wood Sci. Technol.*, 1967. **1**(1): p. 45-70.
  17. Hannuksela, T. and Herve, C., *NMR structural determination of dissolved O-acetylated galactoglucomannan isolated from spruce thermomechanical pulp*. *Carbohydr. Res.*, 2004. **339**: p. 301-312.
  18. Thornton, J., Ekman, R., Holmbom, B., and Örså, F., *Polysaccharides dissolved from Norway spruce in thermomechanical pulping and peroxide bleaching*. *J. Wood Chem. Technol.*, 1994. **14**(2): p. 159-175.
  19. Finnie, S. and Atwell, W.A., *Chapter 1 - Wheat*, in *Wheat Flour*. 2016, AACC International Press. p. 1-16.
  20. Apprich, S., Tirpanalan, Ö., Hell, J., Reisinger, M., Böhmendorfer, S., Siebenhandl-Ehn, S., Novalin, S., and Kneifel, W., *Wheat bran-based biorefinery 2: Valorization of products*. *LWT - Food Sci. Technol.*, 2014. **56**(2): p. 222-231.
  21. Li, W., Cui, S.W., and Kakuda, Y., *Extraction, fractionation, structural and physical characterization of wheat  $\beta$ -d-glucans*. *Carbohydr. Polym.*, 2006. **63**(3): p. 408-416.
  22. Ring, S.G. and Selvendran, R.R., *Isolation and analysis of cell wall material from beeswing wheat bran (*Triticum aestivum*)*. *Phytochemistry*, 1980. **19**(8): p. 1723-1730.
  23. Izydorczyk, M.S. and Biliaderis, C.G., *Cereal arabinoxylans: advances in structure and physicochemical properties*. *Carbohydr. Polym.*, 1995. **28**(1): p. 33-48.

24. Kataoka, M., Wiboonsirikul, J., Kimura, Y., and Adachi, S., *Properties of Extracts from Wheat Bran by Subcritical Water Treatment*. Food Sci. Technol. Res., 2008. **14**(6): p. 553-553.
25. Ruthes, A.C., Martinez-Abad, A., Tan, H.-T., Bulone, V., and Vilaplana, F., *Sequential fractionation of feruloylated hemicelluloses and oligosaccharides from wheat bran using subcritical water and xylanolytic enzymes*. Green Chem., 2017. **19**(8): p. 1919-1931.
26. Ek, M., Gellerstedt, G., and Henriksson, G., *Volume 1 Wood Chemistry and Wood Biotechnology*. 2009.
27. Lawoko, M., Henriksson, G., and Gellerstedt, G., *Characterisation of lignin-carbohydrate complexes (LCCs) of spruce wood (Picea abies L.) isolated with two methods*. Holzforschung, 2006. **60**(2): p. 156-161.
28. Doherty, W.O.S., Mousavioun, P., and Fellows, C.M., *Value-adding to cellulosic ethanol: Lignin polymers*. Ind. Crops Prod., 2011. **33**(2): p. 259-276.
29. Becker, G., *Über den Eiweiß-Gehalt von Nadelhölzern*. Holz als Roh- und Werkstoff, 1962. **20**(9): p. 368-375.
30. Ridley, B.L., O'Neill, M.A., and Mohnen, D., *Pectins: Structure, biosynthesis, and oligogalacturonide-related signaling*. Phytochemistry, 2001. **57**(6): p. 929-967.
31. Smeds, A., Češková, I., Eklund, P., and Willför, S., *Identification of new lignans in Norway spruce knotwood extracts*. Holzforschung, 2012. **66**(5): p. 553-567.
32. Vassilev, S.V., Vassileva, C.G., Song, Y.-C., Li, W.-Y., and Feng, J., *Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion*. Fuel, 2017. **208**: p. 377-409.
33. Schulze, E., *Zur Kenntniss der chemischen Zusammensetzung der pflanzlichen Zellmembranen*. Berichte der deutschen chemischen Gesellschaft, 1891. **24**(2): p. 11.
34. Annison, G., Choct, M., and Cheetham, N.W., *Analysis of wheat arabinoxylans from a large-scale isolation*. Carbohydr. Polym., 1992. **19**(3): p. 151-159.
35. Cebreiros, F., Guigou, M.D., and Cabrera, M.N., *Integrated forest biorefineries: Recovery of acetic acid as a by-product from eucalyptus wood hemicellulosic hydrolysates by solvent extraction*. Ind. Crops Prod., 2017. **109**(Supplement C): p. 101-108.
36. Bergmans, M.E.F., Beldman, G., Gruppen, H., and Voragen, A.G.J., *Optimisation of the Selective Extraction of (Glucurono)arabinoxylans from Wheat Bran: Use of Barium and Calcium Hydroxide Solution at Elevated Temperatures*. J. Cereal Sci., 1996. **23**(3): p. 235-245.

37. Bataillon, M., Mathaly, P., Nunes Cardinali, A.P., and Duchiron, F., *Extraction and purification of arabinoxylan from destarched wheat bran in a pilot scale*. Ind. Crops Prod., 1998. **8**(1): p. 37-43.
38. Glasser, W.G., Kaar, W.E., Jain, R.K., and Sealey, J.E., *Isolation options for non-cellulosic heteropolysaccharides (HetPS)*. Cellulose, 2000. **7**(3): p. 299-317.
39. Jacquemin, L., Mogni, A., Zeitoun, R., Guinot, C., Sablayrolles, C., Saulnier, L., and Pontalier, P.-Y., *Comparison of different twin-screw extraction conditions for the production of arabinoxylans*. Carbohydr. Polym., 2015. **116**: p. 86-94.
40. Fengel, D. and Strobel, C., *FTIR spectroscopic studies on the heterogeneous transformation of cellulose I into cellulose II*. Acta Polym., 1994. **45**(4): p. 319-324.
41. Peng, F., Ren, J.-L., Xu, F., Bian, J., Peng, P., and Sun, R.-C., *Comparative Study of Hemicelluloses Obtained by Graded Ethanol Precipitation from Sugarcane Bagasse*. J. Agric. Food. Chem., 2009. **57**(14): p. 6305-6317.
42. Hägglund, P., Lindberg, B., and McPherson, J., *Dimethylsulphoxide, a Solvent for Hemicelluloses*. Acta Chem. Scand., 1956. **10**: p. 1160-1164.
43. Stoffel, R.B., Neves, P.V., Felissia, F.E., Ramos, L.P., Gassa, L.M., and Area, M.C., *Hemicellulose extraction from slash pine sawdust by steam explosion with sulfuric acid*. Biomass Bioenergy, 2017. **107**: p. 93-101.
44. Luo, X., He, P., and Lin, X., *The mechanism of sodium hydroxide solution promoting the gelation of Konjac glucomannan (KGM)*. Food Hydrocoll., 2013. **30**(1): p. 92-99.
45. Wigell, A., Brelid, H., and Theliander, H., *Degradation/dissolution of softwood hemicellulose during alkaline cooking at different temperatures and alkali concentrations*. Nord. Pulp Pap. Res. J., 2007. **22**(4): p. 488-494.
46. Jones, J.K.W., Wise, L.E., and Jappe, J.P., *The action of alkali containing metabolates on wood cellulose*. Tappi, 1956. **39**: p. 139-141.
47. Scott, R.W., *Influence of cations and borate on the alkaline extraction of xylan and glucomannan from pine pulps*. J. Appl. Polym. Sci., 1989. **38**(5): p. 907-914.
48. Huang, F. and Ragauskas, A., *Extraction of Hemicellulose from Loblolly Pine Woodchips and Subsequent Kraft Pulping*. Ind. Eng. Chem. Res., 2013. **52**(4): p. 1743-1749.
49. Ebringerova, A. and Heinze, T., *Xylan and xylan derivatives - biopolymers with valuable properties, 1. Naturally occurring xylnans structures, isolation procedures and properties*. Macromol. Rapid Commun., 2000. **21**(9): p. 542-556.

50. Mašura, M., *Prehydrolysis of beechwood*. Wood Sci. Technol., 1987. **21**(1): p. 89.
51. Song, T., Pranovich, A., and Holmbom, B., *Characterisation of Norway spruce hemicelluloses extracted by pressurised hot-water extraction (ASE) in the presence of sodium bicarbonate*. Holzforschung, 2011. **65**(1): p. 35-42.
52. Song, T., Pranovich, A., Summerskiy, I., and Holmbom, B., *Extraction of galactoglucomannan from spruce wood with pressurised hot water*. Holzforschung, 2008. **62**: p. 659-666.
53. Örså, F., Holmbom, B., and Thornton, J., *Dissolution and dispersion of spruce wood components into hot water*. Wood Sci. Technol., 1997. **31**(4): p. 279-290.
54. Biermann, C.J., *3 - Pulping Fundamentals*, in *Handbook of Pulping and Papermaking (Second Edition)*. 1996, Academic Press: San Diego. p. 55-100.
55. Ek, M., Gellerstedt, G., and Henriksson, G., *Volume 2 Pulping Chemistry and Technology*. 2016.
56. Fernando, D., Muhić, D., Engstrand, P., and Daniel, G., *Fundamental understanding of pulp property development under different thermomechanical pulp refining conditions as observed by a new Simons' staining method and SEM observation of the ultrastructure of fibre surfaces*. Holzforschung, 2011. **65**(6): p. 777-786.
57. Murton, K. and Duffy, G., *The Influence of Pulp Residence Time on Refining Intensity and Pulp Quality*. Appita J., 2005. **58**(1): p. 64-71.
58. Lawther, J.M., Sun, R.C., and Banks, W.B., *Extraction, Fractionation, and Characterization of Structural Polysaccharides from Wheat-Straw*. J. Agric. Food. Chem., 1995. **43**(3): p. 667-675.
59. Gulbrandsen, T.A., Johnsen, I.A., Opedal, M.T., Toven, K., Oyaas, K., Pranovich, A., Mikkola, J.-P., and Hoff, B.H., *Extracting hemicelluloses from softwood and bagasse as oligosaccharides using pure water and microwave heating*. Cellul. Chem. Technol., 2015. **49**(2): p. 117-126.
60. Hromádková, Z., Košťálová, Z., and Ebringerová, A., *Comparison of conventional and ultrasound-assisted extraction of phenolics-rich heteroxylans from wheat bran*. Ultrason. Sonochem., 2008. **15**(6): p. 1062-1068.
61. Krawczyk, H., Persson, T., Jönsson, A.-S., and Andersson, A., *Isolation of hemicelluloses from barley husks*. Food Bioprod. Process., 2008. **86**: p. 31-36.

62. Roos, A.A., Persson, T., Krawczyk, H., Zacchi, G., and Stålbrand, H., *Extraction of water-soluble hemicelluloses from barley husks*. *Bioresour. Technol.*, 2009. **100**: p. 763–769.
63. Berk, Z., *Chapter 8 - Filtration and Expression*, in *Food Process Engineering and Technology (Second Edition)*. 2013, Academic Press: San Diego. p. 217-240.
64. Sparks, T. and Chase, G., *Section 5 - Solid–Liquid Filtration – Examples of Processes*, in *Filters and Filtration Handbook (Sixth Edition)*. 2016, Butterworth-Heinemann: Oxford. p. 297-359.
65. Öhman, F., Wallmo, H., and Theliander, H., *Precipitation and filtration of lignin from black liquor of different origin*. *Nord. Pulp Pap. Res. J.*, 2007. **22**(2): p. 188-193.
66. Peng, F., Peng, P., Xu, F., and Sun, R.-C., *Fractional purification and bioconversion of hemicelluloses*. *Biotechnol. Adv.*, 2012. **30**(4): p. 879-903.
67. Al-Rudainy, B., Galbe, M., Schagerlöf, H., and Wallberg, O., *Separation of galactoglucomannan from lignin–carbohydrate complexes and lignosulfonates using anti-solvent precipitation of ultrafiltrated spent sulfite liquor*. Manuscript, 2018.
68. Zasadowski, D., Yang, J., Edlund, H., and Norgren, M., *Antisolvent precipitation of water-soluble hemicelluloses from TMP process water*. *Carbohydr. Polym.*, 2014. **113**: p. 411-419.
69. Song, T., Pranovich, A., and Holmbom, B., *Separation of polymeric galactoglucomannans from hot-water extract of spruce wood*. *Bioresour. Technol.*, 2013. **130**: p. 198-203.
70. Persson, T., Nordin, A.-K., Zacchi, G., and Jönsson, A.-S., *Economic evaluation of isolation of hemicelluloses from process streams from thermo-mechanical pulping of spruce*. *Appl. Biochem. Biotechnol.*, 2007. **136-140**: p. 741-752.
71. Krawczyk, H. and Jönsson, A.S., *Separation of dispersed substances and galactoglucomannan in thermomechanical pulp process water by microfiltration*. *Sep. Purif. Technol.*, 2011. **79**(1): p. 43-49.
72. Krawczyk, H., Arkell, A., and Jönsson, A.-S., *Impact of prefiltration on membrane performance during isolation of hemicelluloses extracted from wheat bran*. *Sep. Purif. Technol.*, 2013. **116**: p. 192-198.
73. Cardew, P.T. and le, M.S., *Chapter 2 Membrane Technologies*, in *Membrane Processes: A Technology Guide*. 1998, The Royal Society of Chemistry.
74. 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. Sep. Purif. Technol.*, 2013. **118**(0): p. 387-393.
75. Persson, T. and Jönsson, A.-S., *Fouling of Ultrafiltration Membranes during Isolation of Hemicelluloses in the Forest Industry*. Scholarly Res. Exc., 2009. **2009**: p. 1-7.
  76. Persson, T. and Jönsson, A.-S., *Isolation of hemicelluloses by ultrafiltration of thermomechanical pulp mill process water - Influence of operating conditions*. Chem. Eng. Res. Des., 2010. **88**: p. 1548-1554.
  77. Arkell, A., Vrgoc, F., and Jönsson, A.S., *Back-pulsing as an energy-saving method in the microfiltration of milk*. Int. Dairy J., 2014. **35**(1): p. 1-5.
  78. Väisänen, P., Bird, M.R., and Nyström, M., *Treatment of UF Membranes with Simple and Formulated Cleaning Agents*. Food Bioprod. Process., 2002. **80**(2): p. 98-108.
  79. Koivula, E., Kallioinen, M., Sainio, T., Antón, E., Luque, S., and Mänttari, M., *Enhanced membrane filtration of wood hydrolysates for hemicelluloses recovery by pretreatment with polymeric adsorbents*. Bioresour. Technol., 2013. **143**: p. 275-281.
  80. Andersson, A., Persson, T., Zacchi, G., Stålbrand, H., and Jönsson, A.-S., *Comparison of diafiltration and size-exclusion chromatography to recover hemicelluloses from process water from thermo-mechanical pulping of spruce*. Appl. Biochem. Biotechnol., 2007. **136-140**: p. 971-983.
  81. Schwartz, T. and Lawoko, M., *Removal of acid-soluble lignin from biomass extracts using Amberlite XAD-4 resin*. BioResources 2010. **5**(4): p. 2337-2347.
  82. Westerberg, N., Sunner, H., Helander, M., Henriksson, G., Lawoko, M., and Rasmusson, A., *Separation of galactoglucomannans, lignin, and lignin-carbohydrate complexes from hot-water-extracted Norway spruce by cross-flow filtration and adsorption chromatography*. Bioresources, 2012. **7**(4): p. 4501-4516
  83. Berk, Z., *Chapter 10 - Membrane Processes*, in *Food Process Engineering and Technology (Second Edition)*. 2013, Academic Press: San Diego. p. 259-285.
  84. Cheryan, M., *Ultrafiltration and microfiltration handbook*. 1998: Technomic Publishing Co, Inc.
  85. Nordin, A.-K. and Jönsson, A.-S., *Flux decline along the flow channel in tubular ultrafiltration modules*. Chem. Eng. Res. Des., 2009. **87**: p. 1551-1561.
  86. Yeh, H.M., Wu, H.P., and Dong, J.F., *Effects of design and operating parameters on the declinations of permeate flux for membrane*

- ultrafiltration along hollow-fiber modules*. J. Membr. Sci., 2003. **213**: p. 33-44.
87. Horvath, C., Solomon, B.A., and Engasser, J.-M., *Measurement of Radial Transport in Slug Flow Using Enzyme Tubes*. Ind. Eng. Chem. Fundam., 1973. **12**(4): p. 431-439.
  88. Cui, Z.F. and Wright, K.I.T., *Gas—liquid two-phase cross-flow ultrafiltration of BSA and dextran solutions*. J. Membr. Sci., 1994. **90**(1): p. 183-189.
  89. Taha, T., Cheong, W.L., Field, R.W., and Cui, Z.F., *Gas-sparged ultrafiltration using horizontal and inclined tubular membranes – A CFD study*. J. Membr. Sci., 2006. **279**(1-2): p. 487-494.
  90. Fadaei, H., Tabaei, S.R., and Roostaazad, R., *Comparative assessment of the efficiencies of gas sparging and back-flushing to improve yeast microfiltration using tubular ceramic membranes*. Desalination, 2007. **217**(1-3): p. 93-99.
  91. Hwang, K.J. and Hsu, C.E., *Effect of gas–liquid flow pattern on air-sparged cross-flow microfiltration of yeast suspension*. Chem. Eng. J., 2009. **151**(1-3): p. 160-167.
  92. Aslam, M., Charfi, A., Lesage, G., Heran, M., and Kim, J., *Membrane bioreactors for wastewater treatment: A review of mechanical cleaning by scouring agents to control membrane fouling*. Chem. Eng. J., 2017. **307**: p. 897-913.
  93. Mänttari, M., Al Manasrah, M., Strand, E., Laasonen, H., Preis, S., Puro, L., Xu, C., Kisonen, V., Korpinen, R., and Kallioinen, M., *Improvement of ultrafiltration performance by oxidation treatment in the recovery of galactoglucomannan from wood autohydrolyzate*. Sep. Purif. Technol., 2015. **149**: p. 428-436.
  94. Al-Amoudi, A.S., *Factors affecting natural organic matter (NOM) and scaling fouling in NF membranes: A review*. Desalination, 2010. **259**(1): p. 1-10.
  95. Puro, L., Tanninen, J., and Nyström, M., *Analyses of organic foulants in membranes fouled by pulp and paper mill effluent using solid-liquid extraction*. Desalination, 2002. **143**(1): p. 1-9.
  96. Puro, L., Kallioinen, M., Mänttari, M., and Nyström, M., *Evaluation of behavior and fouling potential of wood extractives in ultrafiltration of pulp and paper mill process water*. J. Membr. Sci., 2011. **368**(1): p. 150-158.
  97. Puro, L., *Identification of extractives and polysaccharides as foulants in membrane filtration of pulp and paper mill effluents 2011*, Doctoral Thesis, Lappeenranta University of Technology: Lappeenranta. p. 106.

98. Carlsson, Dal-Cin, M.M., Black, and Lick, *A surface spectroscopic study of membranes fouled by pulp mill effluent*. J. Membrane Sci., 1998. **142**: p. 1-11.
99. Paugam, L., Delaunay, D., and Rabiller-Baudry, M., *Cleaning efficiency and impact on production fluxes of oxidising disinfectants on a pes ultrafiltration membrane fouled with proteins*. Food Bioprod. Process., 2010. **88**(4): p. 425-429.
100. Argüello, M.A., Álvarez, S., Riera, F.A., and Álvarez, R., *Enzymatic cleaning of inorganic ultrafiltration membranes used for whey protein fractionation*. J. Membr. Sci., 2003. **216**(1): p. 121-134.
101. Steiger, E. and Schulze, E., *Ueber den Furfurol gebenden Bestandtheil der Weizen und Roggenkleie*. Berichte der deutschen chemischen Gesellschaft, 1890. **23**(2): p. 3110-3113.
102. Norris, F.W. and Preece, I.A., *Studies on hemicelluloses: The hemicelluloses of wheat bran*. Biochem. J., 1930. **24**(1): p. 59-66.
103. Jacquemin, L., Mogni, A., Zeitoun, R., Guinot, C., Sablayrolles, C., Saulnier, L., and Pontalier, P.-Y., *Performance evaluation of a semi-industrial production process of arabinoxylans from wheat bran*. Process Biochem., 2015. **50**(4): p. 605-613.
104. Aguedo, M., Ruiz, H.A., and Richel, A., *Non-alkaline solubilization of arabinoxylans from destarched wheat bran using hydrothermal microwave processing and comparison with the hydrolysis by an endoxylanase*. Chem. Eng. Process. Process Intensif., 2015. **96**: p. 72-82.
105. Swennen, K., Courtin, C.M., Lindemans, G.C.J.E., and Delcour, J.A., *Large-scale production and characterisation of wheat bran arabinoxylooligosaccharides*. J. Sci. Food Agric., 2006. **86**(11): p. 1722-1731.
106. Hollmann, J. and Lindhauer, M.G., *Pilot-scale isolation of glucuronoarabinoxylans from wheat bran*. Carbohydr. Polym., 2005. **59**(2): p. 225-230.
107. Krawczyk, H., Arkell, A., and Jönsson, A.S., *Membrane performance during ultrafiltration of a high-viscosity solution containing hemicelluloses from wheat bran*. Sep. Purif. Technol., 2011. **83**: p. 144-150.
108. Jacquemin, L., Zeitoun, R., Sablayrolles, C., Pontalier, P.-Y., and Rigal, L., *Evaluation of the technical and environmental performances of extraction and purification processes of arabinoxylans from wheat straw and bran*. Process Biochem., 2012. **47**(3): p. 373-380.
109. Fillaudeau, L., Blanpain-Avet, P., and Daufin, G., *Water, wastewater and waste management in brewing industries*. J. Clean. Prod., 2006. **14**(5): p. 463-471.

110. Hinge, M. and Christensen, M.L., *Non-ionic soft materials influence on filtration resistance and cake dry matter content*. *AIChE J.*, 2017. **63**(6): p. 2241-2247.
111. Niño-Medina, G., Carvajal-Millán, E., Rascon-Chu, A., Marquez-Escalante, J.A., Guerrero, V., and Salas-Muñoz, E., *Feruloylated arabinoxylans and arabinoxylan gels: structure, sources and applications*. *Phytochemistry Reviews*, 2010. **9**(1): p. 111-120.
112. Roy, C., Budtova, T., and Navard, P., *Rheological Properties and Gelation of Aqueous Cellulose–NaOH Solutions*. *Biomacromolecules*, 2003. **4**(2): p. 259-264.
113. Sur, H.W. and Cui, Z., *Experimental study on the enhancement of yeast microfiltration with gas sparging*. *J. Chem. Technol. Biotechnol.*, 2001. **76**: p. 477-484.
114. Cui, Z.F. and Wright, K.I.T., *Flux enhancements with gas sparging in downwards crossflow ultrafiltration: performance and mechanism*. *J. Membr. Sci.*, 1996. **117**(1): p. 109-116.
115. Arkell, A., Krawczyk, H., and Jönsson, A.-S., *Influence of heat pretreatment on ultrafiltration of a solution containing hemicelluloses extracted from wheat bran*. *Sep. Purif. Technol.*, 2013: p. 46-50.
116. Klinke, H.B., Ahring, B.K., Schmidt, A.S., and Thomsen, A.B., *Characterization of degradation products from alkaline wet oxidation of wheat straw*. *Bioresour. Technol.*, 2002. **82**(1): p. 15-26.
117. Banerjee, S., Sen, R., Mudliar, S., Pandey, R.A., Chakrabarti, T., and Satpute, D., *Alkaline peroxide assisted wet air oxidation pretreatment approach to enhance enzymatic convertibility of rice husk*. *Biotechnol. Progr.*, 2011. **27**(3): p. 691-697.
118. Holloway, W.D., Lelievre, J., and Richards, E.L., *Effects of delignification and of N-methylmorpholine N-oxide treatments on properties of wheat-bran arabinoxylans*. *Carbohydr. Res.*, 1985. **143**: p. 271-274.
119. Hromádková, Z., Paulsen, B.S., Polovka, M., Košťálová, Z., and Ebringerová, A., *Structural features of two heteroxylan polysaccharide fractions from wheat bran with anti-complementary and antioxidant activities*. *Carbohydr. Polym.*, 2013. **93**(1): p. 22-30.
120. Qingxian, M., Liulian, H., and Lihui, C., *Advances in the Control of Dissolved and Colloidal Substances Present in Papermaking Processes: A Brief Review*. *BioResources*, 2013. **8**(1): p. 1431-1455.
121. Pokhrel, D. and Viraraghavan, T., *Treatment of pulp and paper mill wastewater—a review*. *Sci. Total Environ.*, 2004. **333**(1): p. 37-58.

122. Sundberg, K., Holmbom, B., Eckerman, C., and Adams, M., *Method for recovering non-fibrous substances from wood material*. 2002, Google Patents.
123. Willför, S., Rehn, P., Sundberg, A., Sundberg, K., and Holmbom, B., *Recovery of water-soluble acetylgalactoglucomannans from mechanical pulp of spruce*. Tappi J., 2003. **2**(11): p. 27-32.
124. Persson, T., Krawczyk, H., Nordin, A.-K., and Jönsson, A.-S., *Fractionation of process water in thermomechanical pulp mills*. Bioresource Technol., 2010. **101**: p. 3884-3892.
125. Stack, K., Lee, R., Richardson, D., Lewis, T., and Garnier, G., *Complex formation and stability of colloidal wood resin pitch suspensions with hemicellulose polymers*. Colloids Surf. A Physicochem. Eng. Asp., 2014. **441**: p. 101-108.
126. Karlberg, A.-T. and Gäfvert, E., *Extractives in mechanical pulp can cause allergic contact dermatitis*. Nord. Pulp Pap. Res. J., 1996. **11**(2): p. 070-073.
127. Sainio, T., Kallioinen, M., Nakari, O., and Mänttari, M., *Production and recovery of monosaccharides from lignocellulose hot water extracts in a pulp mill biorefinery*. Bioresour. Technol., 2013. **135**: p. 730-737.
128. Allen, L.H., *Characterization of colloidal wood resin in newsprint pulps*. Colloid. Polym. Sci., 1979. **257**(5): p. 533-538.
129. Persson, T., *Extraction and Isolation of Hemicelluloses from Agricultural and Forestry Waste Streams*, 2009, Doctoral Thesis: Department of Chemical Engineering, Lund University.
130. Xu, C., Willför, S., Sundberg, K., Petterson, C., and Holmbom, B., *Physico-chemical characterization of spruce galactoglucomannan solutions: Stability, surface activity and rheology*. Cellul. Chem. Technol., 2007. **41**(1): p. 51-62.
131. Mate, D.M. and Alcalde, M., *Laccase: a multi-purpose biocatalyst at the forefront of biotechnology*. Microb. Biotechnol., 2017. **10**(6): p. 1457-1467.
132. Mayer, A.M. and Staples, R.C., *Laccase: new functions for an old enzyme*. Phytochemistry, 2002. **60**(6): p. 551-565.
133. Krawczyk, H., Oinonen, P., and Jönsson, A.-S., *Combined membrane filtration and enzymatic treatment for recovery of high molecular mass hemicelluloses from chemithermomechanical pulp in process water*. Chem. Eng. J., 2013. **225**: p. 292-299.
134. Oinonen, P., Areskog, D., and Henriksson, G., *Enzyme catalyzed cross-linking of spruce galactoglucomannan improves its applicability in barrier films*. Carbohydr. Polym., 2013. **95**(2): p. 690-696.

135. Ko, C.-H. and Fan, C., *Enhanced chemical oxygen demand removal and flux reduction in pulp and paper wastewater treatment using laccase-polymerized membrane filtration*. J. Hazard. Mater., 2010. **181**(1): p. 763-770.
136. Merin, U., Gésan-Guiziou, G., Boyaval, E., and Daufin, G., *Cleaning-in-place in the dairy industry: criteria for reuse of caustic (NaOH) solutions*. Lait, 2002. **82**(3): p. 357-366.
137. Seider, W.D., Seader, J.D., Lewin, D.R., and Widagdo, S., *Product and Process Design Principles : Synthesis, Analysis, and Evaluation*. 3 ed. 2010, Hoboken, NJ, USA: Donald Fowley.
138. Everts, H.J., Maastricht, E.v., and Folz, R. *+Flux a new approach in beer membrane filtration*. Paper presented at the 11th International Congress on Membranes and Membrane Processes. 2017. San Francisco