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UNIVERSITY OF TECHNOLOGY

Faculty of Technology
Master's Degree Programme in Chemical and Process Engineering

RECOVERY OF HEMICELLULOSES FROM WOOD HYDROLYSATES BY MEMBRANE FILTRATION

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ABSTRACT

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Hemicelluloses are among the most important natural resources that contain polysaccharides. In this study the separation and purification of hemicelluloses from water extraction liquors containing wood hemicelluloses, lignin compounds and monosaccharide by using membrane filtration was investigated. The isolation of the hemicelluloses from the wood hydrolysates was performed in two steps: concentration of high molar mass hemicelluloses by ultrafiltration and separation of low molar mass hemicelluloses from monomeric sugars using tight ultrafiltration membranes. The purification of the retained hemicelluloses was performed by diafiltration.

During the filtration experiments, the permeate flux through ultrafiltration and tight ultrafiltration membranes was relatively high. The fouling ability of the used membranes was relatively low. In our experiments, the retention of hemicelluloses using two filtration steps was almost complete. The separation of monosaccharides from hemicelluloses was relatively high and the purification of hemicelluloses by diafiltration was highly efficient. The separation of lignin from hemicelluloses was partially achieved. Diafiltration showed potential to purify retained hemicelluloses from lignin and other organics. The best separation of lignin from hemicelluloses in the first filtration step was obtained using the UC005 membrane. The GE-5 and ETNA01PP membranes showed potential to purify and separate lignin from hemicelluloses. However, the feed solution of the second filtration stages (from different ultrafiltration membranes) affected the permeate flux and the separation of various extracted compounds from hemicelluloses. The GE-5 and ETNA01PP membranes gave the efficient purification of the hemicelluloses when using diafiltration.

Separation of degraded xylan from glucomannan (primary spruce hemicelluloses) was also possible using membrane filtration. The best separation was achieved using the GE-5 membrane. The retention of glucomannan was three times higher than xylan retention.

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Mohammad AL Manasrah

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ABBREVIATION

AcGGM	O-Acetyl-GalactoGlucoMannan
CA	Cellulose Acetate
CE	Capillary Electrophoresis
DP	Degree of Polymerization
DMSO	Dimethyl Sulfoxide
GC	Gas Chromatography
GGM	GalactoGlucoMannan
GPC	Gel Permeation Chromatography
HCW	Hot Compressed Water
HPSEC	High Performance Size Exclusion Chromatography
HPAEC-PAD	High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection
HW	Hard Woods
HWP-E	Hot Water Pre-Extraction
LC	Liquid Chromatography
MALDI-TOF-MS	Matrix Assisted Laser Desorption / Ionization Time of Flight Mass Spectrometry
MF	Microfiltration
M_n	Number Average Molar Mass
M_w	Weight Average Molar Mass
MM	Molar Mass
NF	Nanofiltration
NIR	Near Infrared
NMR	Nuclear Magnetic Resonance
PHWE	Pressurized Hot Water Extraction
PLPW	Pressurized Low-Polarity Water
PP	PolyPropylene
PSO	PolySulfone
PWF	Pure Water Flux
PWP	Pure Water Permeability
Py-GC-MS	Pyrolysis – Gas Chromatography-Mass Spectrometry
RO	Reverse Osmosis
SCFs	Sub-Critical Fluids
SDS	Sodium Dodecyl Sulfate
SFE	Supercritical Fluid Extraction
SPME	Solid-Phase Micro-Extraction
SW	Soft Woods
SWC	Super-heated Water Chromatography
TMP	Thermo-Mechanical Pulping
TUF	Tight Ultrafiltration
UF	Ultrafiltration

LITERATURE REVIEW

1. INTRODUCTION

The major chemical structural components of all wood species polymeric matrix are: carbohydrates (mainly polysaccharides such as cellulose and hemicelluloses) and lignin. Hemicelluloses are among the most plentiful natural resources that contain polysaccharides. They exist in different compositions and structures as a second biopolymer in many lignocellulosic biomass materials. Hemicelluloses offer important and renewable raw material source for several industrial processes. In recent years, great interest has been directed to hemicelluloses as polymers for various chemical, biotechnological and pharmaceutical applications. Several economic and environmental benefits can be obtained from utilization wood and crop residue hemicelluloses. The hydrolysis of hemicelluloses and fermentation of hydrolysates to ethanol has been promoted as an environmentally sustainable process to utilize material that would otherwise be wasted. Therefore the recovery of hemicelluloses from different biomasses especially from wood will be one of the most interesting industrial processes in the near future.

Different separation and purification procedures have been proposed to isolate hemicelluloses from different raw materials. Extraction of hemicelluloses from different resources has been studied since long time ago. Isolation of hemicelluloses using cost efficient extraction methods would be beneficial to increase the utilization of hemicelluloses. Alkaline aqueous solutions and organic solvents have been used to extract hemicelluloses from the original or delignified wood (holocellulose). Some hemicelluloses can be extracted from wood using hot water. Moreover, water can partly extract depolymerized hemicelluloses from steam treated wood. Nowadays, pressurized hot water can be an attractive alternative as environmentally friendly solvent for extraction hemicellulose from its resources.

Pressure driven membrane filtration can be used for the separation and concentration of hemicelluloses extracted from wood. The concentration and purity of the isolated hemicelluloses has to be sufficient to use them for different applications. Those membrane processes are generally classified into the following categories: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Cut-off of the membrane is the major difference between each of these classes. Membranes with proper cut off and porosity show substantial separation performance. Membrane technology can provide a promising alternative method for the concentration and purification hemicelluloses from different process solvents. Low energy demand makes the membrane separation competitive compared with other separation technologies. This technology can be tailored to get proper degree of purification.

In this work, hemicelluloses were firstly extracted from wood chips or saw dust by using pressurized hot water. The extraction liquor was then concentrated and the retained hemicelluloses was purified by membrane filtration. Several different membranes were performed to find the most suitable membrane material, cut off, and operating conditions for this process. The performance of the used membrane separation processes in terms of permeates flux and retention has been studied.

The specific objectives of this work were:

i. To investigate the use of membrane filtration for concentration and purification of extracted hemicelluloses and polysaccharides.
ii. To evaluate the performance and efficiency of the used membrane separation processes.
iii. To produce hemicelluloses and polysaccharides with high enough concentrations that they can be used for various applications such as bioethanol production.

2.HEMICELLULOSES

Hemicelluloses are among the most plentiful renewable resources on earth. They are one of the main polymeric constituents of biomass such as woods. Hemicelluloses received a lot of attention in the last few decades in terms of novel applications. Different isolation procedures have been performed to separate hemicelluloses from various wood species.

2.1 Structure and Chemical Composition

Hemicelluloses are colorless and relatively stable carbohydrate polymers. They are heteroglycans containing various types of sugar units, arranged in different proportions and with different structures. Hemicelluloses derive from a single sugar (glucose); and they consist of several five and six carbon units none uniformly linked. Wood is the main natural resource of hemicelluloses. The content of hemicelluloses represents 20 -30% of the dry weight of wood, the wood hemicelluloses consist of variety of linkages and branching types depending on the wood tissues [1, 2].

Hemicellulose is a branched polymer that is in principle made of number of sugar units. The structural sugar units of hemicellulose are d-xylose, l-arabinose, d-glucose, d-galactose, d-mannose, d-glucuronic acid, 4-*O*-methyl-d-glucuronic acid, d-galacturonic acid, and to a lesser extent, l-rhamnose, l-fucose, and various *O*-methylated neutral sugars. Some of side chains may also contain acetyl groups of felurate. Main monomers of hemicellulose are shown in Figure 2.1. [1, 2]

Hemicelluloses have relatively low molar mass compared with other wood polymers. The degree of polymerisation of hemicelluloses is around 80–200. The general units of hemicelluloses are pentosans and hexosans of which general formula are $(C_5H_8O_4)_n$ and $(C_6H_{10}O_5)_n$ respectively. [1, 2]

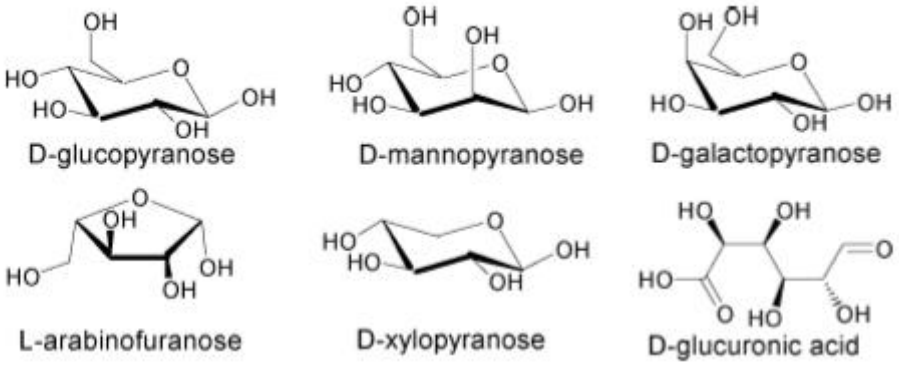


Figure 2.1 : Main Constituents of Hemicelluloses

2.2 Specifications and Major Properties

The molar mass (MM) and the degree of polymerization (DP) are the important properties for hemicelluloses. These properties have been determined by using different analytical approaches which different values of MM and DP . The number average molar mass (M_n) and the weight average molar mass (M_w) are the main molar mass parameters. Osmometry is usually used to measure the number average molar mass where it can be calculated from the ratio between the number of reducing end groups and the total number of sugar residues present in the hemicelluloses. The weight average molar mass (M_w) can be measured by characterizing light-scattering or sedimentation equilibrium [3]. On the other hand the apparent molar mass of the hemicelluloses can be determined by using high-performance size-exclusion chromatography (HPSEC). Wide range of the molar mass magnitude for an individual polysaccharide can be obtained by this method. The hemicelluloses characterization studies have shown that the molar mass range of xylan (main hemicellulose in hardwoods (HW)) is between 16 - 50 kg/mol while the molar mass range of galactoglucomannan (GGM) and arabinogalactan (main hemicelluloses in softwoods (SW)) is between 5 - 30 kg/mol; and 9 - 250 kg/mol respectively. The DP of the softwood O-acetyl-galactoglucomannan (AcGGM) is approximately between 100 and 150, equivalent to a molar mass around 16–24 kg/mol [3, 4, 5].

Different tools have been used to study the main hemicelluloses characteristics. Nuclear magnetic resonance (NMR) spectroscopy is one of the most important non-destructive tools for investigation the structure of polysaccharides. Anomeric configuration and sequence of glycosyl residues can be inspected by using different high-resolution NMR

techniques. In various polysaccharides the distribution of *O*-acetyl groups has also been determined by direct NMR analysis [6, 7].

Jacobs and Dahlman [3] employed the size exclusion chromatography and off-line matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-MS) to determine the molar mass parameters of wood and pulp hemicelluloses. These parameters can be conveniently determined without standards calibration on an absolute molar mass scale. They found that the molar mass parameters of the birch and aspen glucuronoxylans are rather similar to those of the spruce and pine arabinoglucuronoxylans. Sun and Tomkinson [8] investigated the chemical composition and structural characterization of the water-soluble hemicelluloses and lignin from steam exploded birch wood. This study showed that the glucuronxylan in hardwoods has much higher DP values. Their results demonstrated that the nature of the cooking process of pulps has strong effect on the molar mass parameters of extracted hemicelluloses from chemical pulps.

Comparison with cellulose, the chemical and thermal stability of hemicelluloses is generally lower than that of cellulose, presumably due to their lack of crystallinity and lower DP. In addition, hemicelluloses generally differ from cellulose with respect to their solubility in alkali. This characteristic property is the most commonly utilized when fractionating different polysaccharides in lignin free samples. Hemicellulosic fragments of hardwood such as xylan and arabinogalactan especially from larch species are partly or even totally water-soluble. Therefore, in these special cases, the distinction between water-soluble hemicelluloses, sugars (mainly mono and disaccharides), and extractive derived compounds is sometimes complicated [7].

The branched structure and molar mass of hemicelluloses are the key factors that affect on acid hydrolyzation process of hemicelluloses. During hydrolysis at high temperature, losses in acetyl, holocellulose, and lignin contents occurred. Thus, physical properties such as shrinkage and swelling coefficient of hemicelluloses changed. The ratio of sugar units in hemicelluloses highly depend on the extraction and isolation procedures. Preservation the acetyl group in the isolated hemicelluloses is important to maintain theirs water solubility. These groups hinder the formation of the hydrogen bond between

molecules of polysaccharides chains. The alkali-soluble hemicelluloses have different properties than water-soluble hemicelluloses [9].

Most of native GGM isolated from softwoods contain acetyl groups. The degree of acetylation of water-soluble AcGGM from softwoods varies with the used raw materials and method of isolation. The range of the average molar mass for AcGGM extracted by water is between 30 and 60 kg /mol; and the molar mass of spruce AcGGM is in the range of 20-78 kg/mol. The polysaccharides which were extracted by heat or microwave treatment have lower molar masses. The raw materials and the isolation procedure of hemicelluloses are the main parameters that strongly influence the hemicellulose molar mass. Because many polysaccharides have wide molar mass distribution; exact determination of molar mass of some polysaccharides is sometimes difficult [9].

2.3 Sources

Hemicelluloses are polysaccharides that occur together with cellulose in most plant tissues. In woody plants, hemicelluloses constitute approximately one-fourth to one third of the total organic material present. Around 80% of the biomass on earth is lignocellulosic materials. Hemicelluloses are one of the main components of biomass. They exist with a wide variation in content and chemical structure. Hemicelluloses approximately cover 20–40 wt. % for lignocellulosic biomass. Hardwoods, softwoods, grasses, and straws are the major sources of hemicelluloses. Hemicelluloses are also available in the forest industry, energy crops, and agricultural residues. Table 2.1 summarizes number of hemicelluloses sources and their hemicellulose contents [10, 11]

Table 2.1: Contents of Hemicelluloses in Different Sources [10].

Source	Hemicelluloses Fractions (%)
Wheat Straw	33
Sugarcane Bagasse	35
Olive Residue	30
Sugar Beet Pulp	30
Agricultural Residues	27
Woody Crops	30
Municipal Solid Waste	9
Herbaceous Energy Crops	30
Corn Fibers	35

2.4 Major Applications

Hemicelluloses offer promising renewable raw material supply for many industrial processes. Organic acids such as acetic acid, methane, monosaccharide, sugar alcohols, solvents alternatives to petroleum-derived chemicals, and dyes are the potential products can be made from hemicelluloses [9, 12, 13, 14]. Several interesting novel technological applications, such as cationic biopolymers, hydrogels, and long-chain alkyl ester derivatives have been developed in recent years. These technologies use hemicelluloses as raw materials. Hemicelluloses make an important contribution as raw materials for production of fuel grade ethanol. Over the past few decades, the structure and role of hemicelluloses which represent a large proportion of polysaccharides in wood and pulp fibers, have been widely studied [15].

Great interest has been occurred to find new applications of hemicelluloses polymers in chemical, biomedical and pharmaceutical fields. Thus, many potentially useful applications of hemicelluloses as raw materials for food additives, thickeners, emulsifiers, adhesives, binder, anti-tumor agents and adsorbents have attracted attention in the past few years. Microbial enzymes production by acidic hydrolysis of xylan is also one of the possible industrial applications of hemicelluloses. Recently, production of non-carcinogenic sweetener from the reduction of xylose to xylitol has become an attractive

application. Antioxidants are also produced from hemicelluloses hydrolysates of Eucalypyus globules wood [16].

The recent application of O-acetylgalactoglucomannans (Ac GGM) (mannans) is mainly in production of various gum types. Those gums are applied in the food industry as stabilizer and gelling agents. Novel food gum was developed from corn branched heteroxylan. The hemicellulosic gums usually have nutritional, medicinal, and health product applications. Furthermore, guar gum has large market in various areas in textile, paper, explosives, cosmetic, and mining industries [9].

Xylan is utilized in production of furfural or xylitol. Gel forming and thermoplastic materials are also developed in laboratory scale from polymeric xylans. Furthermore xylans have been tested for adsorption onto cellulosic fibers and as a component for paint formulation. Higher valued application in chiral separations and pharmaceuticals are found by using low molar mass xylans. Derivatisation of xylans to ethers and esters is performed to develop new products. However, the development of new applications of hemicelluloses requires constant quality and sufficient quantity for industrial scale processes. Enhanced mechanical properties, flexible structure, and low degradation rate of xylan offer excellent opportunity to use it as thermoplastic-starch composites additives. Its role is to improve the life and properties of bioplastic. In addition, cereal xylans can be used to lower cholesterol in human blood [13, 14, 17, 18].

2.5 Major Recovery Techniques

Various extraction and purification procedures have been proposed to isolate hemicelluloses from different types of woods. Delignification procedure is often utilized to give holocellulose, prior of alkaline extraction of hemicelluloses. Ultrafiltration (UF) can be used for the separation and purification of hemicelluloses extracted from wood and annual crops. Aqueous solutions of several alternative alkaline, neutral or acidic components at elevated temperature and pressure are used to dissolve lignin and some hemicelluloses from wood chips [8, 9, 14, 19]. Microwave oven treatment is used to extract acetyl-galactoglucomannans from spruce [20].

Prior to pulping processes, the extraction of hemicelluloses from wood chips gives great opportunities to utilize extracted hemicelluloses as a biomaterial feedstock or pulp additives. Currently, the spent pulping liquor that contains hemicelluloses from wood chips is burned as a low BTU (British Thermal Unit) value fuel in the recovery boiler. Efficient utilization of the wood component will increase revenue streams for the forest products industry and help to maximize the utilization of biomass in the production of fuels and chemicals. Various benefits are obtained from removal of hemicellulose prior to pulping; it may improve the performance of manufacturing processes of pulp mill, decrease the using of chemicals in pulping and bleaching and possibly leads to reduce environmental effects of sulphur emissions. In an optimized biorefinery, the extraction of fraction of the hemicelluloses is performed prior to pulping processes. Some of the extracted hemicelluloses can be utilized as downstream pulp additives to improve pulp yield and bonding strength. Removal of hemicelluloses reduces cooking chemical usage, and improves recovery boiler throughput [21, 22].

By using different extraction methods, hemicelluloses can be removed from holocellulose and lignocellulosic materials. The isolation of hemicelluloses from the raw or delignified wood (holocellulose) can be performed by alkaline aqueous solutions or organic solvents extraction. DMSO (dimethyl sulfoxide), NaOH, and KOH are usually used for extraction. Polysaccharides with different structures and content are produced depending on the used solvent. Alkaline Extraction or solvent extraction by DMSO can provide polymeric hemicelluloses from woods or annual plants. Polymeric material is easier to concentrate, using precipitation or ultrafiltration. If the extraction method does not deliver concentrated sugars, then reverse osmosis can be used. At the same time, reverse osmosis can separate the acetic acid from the sugars. However, alkaline methods can produce acetate, which will require acid addition and salt formation to derive acetic acid [3, 23].

Water can be used to extract hemicelluloses from a number of wood species such as extraction of arabinogalactan from larch wood. Depolymerized hemicelluloses can be partly extracted from steam treated wood by using water. Dilute acid such as acetic acid can also be used to isolate hemicelluloses from woods. The acid extraction of hemicelluloses produces short oligosaccharides or monomeric sugars [3, 23].

The efficient alkaline extraction of hemicelluloses requires finely ground wood or delignification of the wood. Utilization of DMSO causes wood to swell, so it is used to study the hemicellulose structure. This solvent might be useful in pretreatment where it will allow access to various components of the wood. The study of Palm and Zacchi [20] showed that the hemicelluloses acetylgalactoglucomannan and arabino-4-*O*-ethylglucuronoxylan can be extracted by using microwave treatment. They succeeded to obtain 12.5 g hemicelluloses/100 g of dry wood at 200 °C. Pisarnitskii et al [24] isolated hemicelluloses from oak wood by using aqueous-alcoholic media. They succeeded to extract 40-90% of the total hemicellulose fraction from oak wood.

Janzon et al. [25] used nitren to extract xylans. They found that the birch and eucalyptus are the applicable sources to obtain polymeric xylan. In their nitren extraction experiments 98% of the xylans were isolated from the initial pulps of birch and eucalyptus. The results indicated that the used solvent effect on the mannan extraction from softwoods. The efficiency of the used extraction increases in the following order: Nitren < KOH < NaOH. However, they found that the nitren extraction has the advantage of a much lower chemical load compared to NaOH or KOH.

Membrane filtration has been used to isolate hemicelluloses from process water of thermo-mechanical pulped wood. While ultrafiltration was used to extract hemicelluloses from pulp and paper process water, diafiltration or size-exclusion chromatography (SEC) was used for final purification of hemicelluloses. The overall performance and cost efficiency of the process depend on the performance of the pre-concentration and purification process by ultrafiltration. [26, 27]

2.6 Hemicelluloses Contents in Different Wood Species

The major chemical constituents of all wood species are a polymeric matrix of structural components: carbohydrates (mainly cellulose and hemicelluloses) and lignin together with smaller amounts of pectic substances. Two thirds of the dry wood is composed of polysaccharides; cellulose and various hemicelluloses. The cellulose content is the same in soft and hard woods (40-45% of the dry wood), but softwoods usually contain less hemicelluloses and more lignin [7].

The typical content of hemicelluloses in softwoods is 25%-30% and 30%-35% in hardwoods. The structure of hemicelluloses is different between softwoods and hardwoods. Figure 2.2 summarizes the basic chemical composition differences between Scots pine (Pinus sylvestris) and silver birch (Betula pendula) [7].

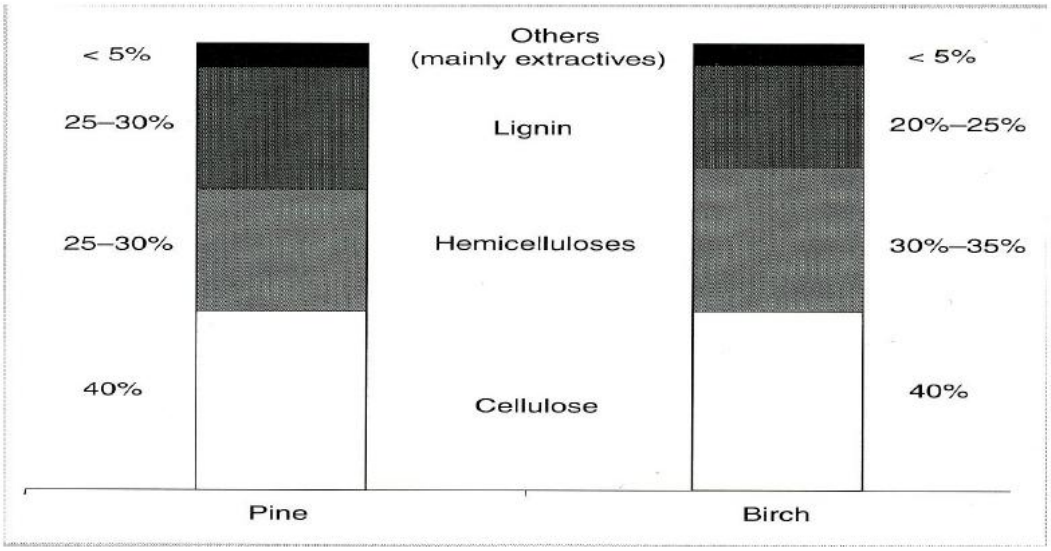


Figure 2.2: Average Chemical Composition of the Dry Solids of Scots Pine (Pinus Sylvestris) and Silver Birch (Betula Pendula). [7]

Softwoods and hardwoods differ not only in the content of total hemicelluloses but also in the percentage of individual hemicellulose constituents (mainly glucomannan and xylan) and the detailed composition of these constituents. It is typical that softwood hemicelluloses have more mannose and galactose units and less xylose units and acetylated hydroxyl groups than those from hardwoods [4, 7].

The primary hemicelluloses of softwood such as spruce and pine are galactoglucomannans (15-20% of the dry wood mass) and arabinoglucuronoxylan (5-10% of the dry wood mass).While the backbone of galactoglucomannans (Figure 2.3) is a linear or slightly branched chain of β-(1→4)-linked D-mannopyranose and D-glucopyranose units, the backbones of arabinoglucuronoxylan is β-(1→4) - linked xylopyranose units. Glucuronoxylan (xylan) (20-30% of the dry wood mass) and glucomannan (<5% of the dry wood mass) are the primary components in hardwood such as birch and aspen. Xylan is more specifically an O-acetyl-4-Omethylglucurono- ß-D-xylan, it backbone consists of β - (1→4)-linked xylopyranose units (Figure 2.4). Unlike softwood xylan, hardwood xylan

does not contain arabinose side chains. Table 2.2 summarizes the main structural features of hemicelluloses appearing in both softwood and hardwood. [4, 7, 28, 29]

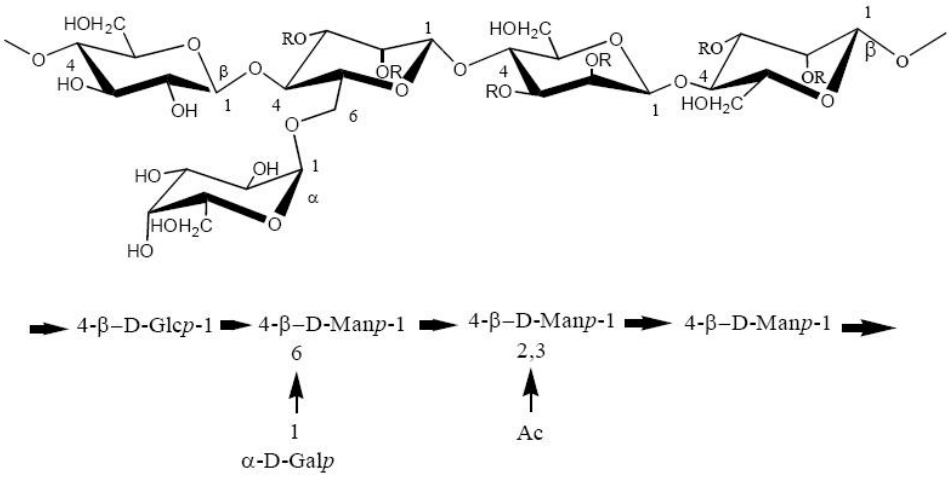


Figure 2.3: Principle Structure of Galactoglucomannans in Softwoods
Sugar units: β-D-glucopyranose (Glc*P*); β-D-mannopyranose (Man*p*); β-D-galactopyranose (Gal*p*). R = CH_3CO or H. The lower representation is the abbreviated formula showing the proportions of the units (galactose-rich fraction) [4].

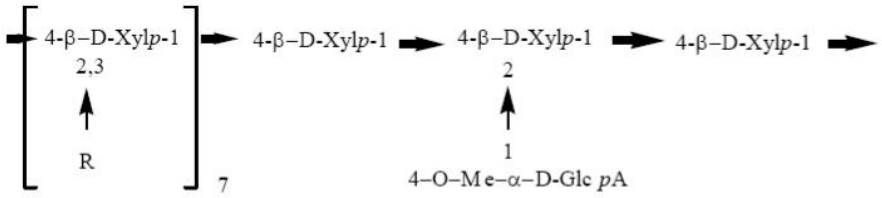


Figure 2.4: Principle Structure of Glucuronoxylan (Xylan) in Hardwoods

Sugar units: β-D-xylopyranose (Xyl*P*); 4-O-methyl-α-D-glucopyranosyluronic acid (Glc*p*A); R = Acetyl group (CH_3CO) [4].

Table 2.2: The Main Structural Features of hemicelluloses in Both Softwood and Hardwood [4].

Wood	Hemicellulose type	Amount (% on wood)	Composition			DP
			Units	Molar ratios	Linkage	
SW	Galacto-glucomannan	5-8	β-D-Man*p* β-D-Glc*p* α-D-Gal*p* Acetyl	3 1 1 1	1 → 4 1 → 4 1 → 6	100
	(Galacto)-glucomannan	10-15	β-D-Man*p* β-D-Glc*p* α-D-Gal*p* Acetyl	4 1 0.1 1	1 → 4 1 → 4 1 → 6	100
	Arabino-glucuronoxylan	7-10	β-D-Xyl*p* 4–O–Me–α-D-Glc*pA* α-L-Araf	10 2 1.3	1 → 4 1 → 2 1 → 3	100
HW	Glucuronoxylan	15-30	β-D-Xyl*p* 4–O–Me–α-D-Glc*pA* Acetyl	10 1 7	1 → 4 1 → 2	200
	Glucomannan	2-5	β-D-Man*p* β-D-Glc*p*	1-2 1	1→ 4 1→ 4	200

3. EXTRACTION OF HEMICELLULOSES

Many processes can remove hemicelluloses from lignocellulose. Firstly, oxidative isolation is used for analytical and structural hemicelluloses studies. Extraction methods by hot water, alkaline, and chemical solvents are currently employed to remove hemicelluloses from holocellulose and lignocellulosic materials. The isolation of hemicelluloses facilitates the study of its structure in polymeric form. In the wood biorefinery, pulp and paper production can be combined with conversion of hemicelluloses to fuels. In the ideal case the lignocellulosic materials that do not end up in the final product would be converted into valuable products and more useful forms of energy and chemicals. High value products can be obtained from extra hemicelluloses and lignin that will not be used in the main biomass processing operation. The ultimate fate of the hemicelluloses and lignins is usually important for the economics and design of the process [23, 30].

3.1 Extraction Methods

Alkaline, acidic, and solvent extraction of hemicelluloses are the general chemical extraction categories that can be applied to isolate hemicelluloses from woods prior to paper manufacturing processes. The alkali treatment is commonly used more than other treatment processes. The environmental pollution is the main drawback of this type of treatment [23]. Gáspár et al. [31] investigated the performance of alkaline treatment in breaking down the bonds between carbohydrates and lignin aiming to enhance enzymatic digestibility of corn fiber. They found that the alkali treatment can be the most promising process to break the ester bonds between lignin, hemicelluose and cellulose without fragmentation of the hemicellulose polymer.

3.1.1. Alkaline Methods

Efficient alkaline extraction of hemicelluloses from wood requires delignification of the ground wood. The purpose of alkaline extraction processes is to release hemicellulose from its sources without any effects on the end product such as paper or chemicals. The yield of extractable sugars from wood chips is usually low. In pulping processes especially kraft pulping, both lignin and hemicellulose fractions will be removed from soft and hard

woods by high temperature alkaline extraction process. The structure and behavior of hemicelluloses, the complexity of used organics, and the sulfur content in the black liquor are the main parameters that influence on the development of the product from the extra hemicelluloses. Acquiring additional valuable products along with the same paper products is the aim of wood chips pretreatment. However, significant removal of mannose might affect on the paper yield. The gentle alkaline treatments are possible to get hemicellulose fraction without lignin contamination [23, 30].

The hemicelluloses content in the produced pulp from the chemi-mechanical pulping process of hardwoods is lower than other pulping processes. This process uses cold soda to produce corrugated board and writing paper. High purity xylose can be produced from hardwoods by cold caustic extraction. The presence of ethylenediamine and monoethyl amine in alkaline solutions produces deliginified pulps with hemicelluloses content higher than kraft with nearly the same kappa number and yield. Some hemicelluloses can be degraded by ammonia fiber explosion. Ammonia pretreatment and lime or other alkaline treatments usually change the lignin structure and also delignify the wood material. However, numbers of limitations such as undesirable damage in the wood fiber impede the applications of alkaline pretreatment of wood chips prior to paper and chemicals production. In some cases, alkaline treatments can be used as apart of solvent extraction [23, 30].

3.1.2 Acidic Methods

Dilute acid pre-hydrolysis has been used in cellulose and hemicellulose degradation. Number of experiments by using acetic acid auto-hydrolysis in treatment of pine and eucalypt provided pulp with low hemicelluloses content. Pre-hydrolysis provides significant hemicellulose content reduction in produced pulps. The hemicelluloses in the end product such as paper and also in their resource such as wood must be tested to investigate the efficiency of this technology. Contamination the hemicellulosic sugars with aromatic compounds is the expected problem during this process. However, the degradation of hemicelluloses is increasing with higher temperatures, longer cooking times, and greater loadings of acetic acid. Generally, the applying of the acid extraction is much better with smaller material [23, 30].

3.1.3 Solvent Methods

Dimethyl sulfoxide (DMSO) is the most common neutral (non-destructive) solvent that has been applied to extract hemicellulose from pulp. The hemicelluloses can be extracted without cleaving the acetyl esters compounds, which is helping to study the hemicellulose structure. The high cost and potential hazard problems with handling large volumes of this solvent are the main reasons that limit the utilization of DMSO solvent in pulping applications [23]. Slightly acidic or neutral (pH 5.5-7) water can be the best solvent for extracting unmodified AcGGM. It is applied to extract AcGGM from pre-swollen holocellulose. Combination of DMSO with water has been used to extract GGM from spruce holocellulose [9, 30].

The preliminary task of the used solvent in wood pretreatment is swelling the wood. The swelling allows access of the solvent in wood components. The solvent can be displaced without reduction and then can be easily recovered. Alcohols, phenols, esters, solvents with acidic and alkaline additions are the examples of different types of solvents that have been tested in wood pretreatment processes. However, the objective of the solvent system is to delignify the ligncellulosic materials, and leave part of hemicelluloses in cellulose-containing fractions for paper making and the other part in degraded lignin fraction for other applications [23, 30].

The aqueous solutions of ethanol and methanol are often used in organosolv processes. These processes are performed at elevated temperatures to degrade and remove lignin contents. The use of other alcohols did not give any better result. Phenol and butanol can get rid of lignin from pine. In some cases neutral alkali earth metal salt was used as solvent methods additive. Divalent cations have shown better results than monovalent and trivalent cations in liberating of hemicelluloses from softwood [23, 30].

3.2 Extraction and Isolation of Hemicelluloses from Lignocellulosic Materials

The isolation of hemicelluloses from various lignocellulosic materials especially woods has been already studied long time ago. Many researchers have studied different methods, solvents, operating conditions and processes for extraction of hemicelluloses. Different properties and solubility of the wood hemicelluloses require design different separation methods. Proper extraction process needs special requirements to fractionate a certain hemicellulose or mixture of hemicelluloses. However, the presence of lignin network as well as ester and ether lignin-carbohydrate linkages limits the hemicellulose extraction from the cell wall matrix of wood. The extensive hydrogen bonds between the individual polysaccharides components also impede their separation [1, 2, 4].

Various researchers have suggested different extraction processes of hemicelluloses from their sources. Geng et al. [32] isolated hemicelluloses from caligonum monogoliacum and tamarix spp by sequential treatments with (60/40, v/v) ethanol-H_2O solution under acid catalyst (0.2 M HCl) at 70 ºC for 4 h and with 2% H_2O_2 at pH 11.5 for 16 h. They used different analysis techniques to study the chemical compositions and physico-chemical properties of the extracted hemicelluloses from both methods. The highest hemicelluloses yield (% dry matters) they obtained was 44.9 % from caligonum monogoliacum and 44.3 % from tamarix spp. The alkaline peroxide post treatment gave a much higher degree of polymerisation with boarder molar mass distribution and higher average molar mass of the extracted hemicelluloses.

Sun et al. [33] used NaOH solution with different concentrations to extract hemicelluloses from dewaxed and partially delignified fast-growing poplar wood. They found when the concentration of NaOH increases the yield of the solubilized hemicelluloses increases. Xylose was the main sugar component in all of the produced hemicelluloses. Rodriguez et al. [34] studied the extraction of oak wood compounds with sub-critical water-ethanol mixtures as extraction solution (0-60% ethanol). Their study showed that the optimum extraction time and temperature were 60 min and 200 ºC respectively.

The direct extraction of hemicelluloses from native wood reduces the chemical modification operations of hemicelluloses. The hemicelluloses are usually extracted from delignified wood (holocellulose) using one or several stages. Acidic sodium chlorite delignification is commonly used before the alkaline extraction of hemicelluloses. Oxidation, hydrolysis, and dehydration of sensitive sugars in the hemicelluloses always occur in delignification processes. At acid conditions, acetyl group can split off. DMSO was used to isolate AcGGM from Parana pine delignified by chlorite [4, 9].

Curling et al. [35] have developed combination between mechanical refining techniques with mild alkaline extraction on a laboratory scale to release hemicellulose in gels type from Sitka spruce. They tested the effect of alkali type and concentration, temperature, addition of hydrogen peroxide as a delignification and purification agent, and borate addition. Their results found that the combination of a mild alkali treatment with addition of hydrogen peroxide offers the effective hemicellulose extraction. The yield of hemicellulose increases as the temperature increases whilst the addition of hydrogen peroxide enhanced the purity. The mission of the addition of borate to the extraction medium was to alter the characteristics of the gel by altering monosaccharide ratio in the formed gel.

Deacetylation of acetyl groups in the wood hemicelluloses especially GGM will occur at alkaline conditions, which explain the lack of acetyl group in extracted hemicelluloses. The deacetylation can occur at pH values 9-10 and temperature below 50 ºC. Furthermore, some hydrolysis of glycosidic bonds and sensitive side groups as well as degradation and decomposition of dissolved polysaccharides will always take place at alkaline conditions. Different fraction of hemicelluloses can be isolated by using various concentrations of sodium and potassium hydroxide in alkaline extraction (successive extractions). The dissolution of GGM can be enhanced by adding borate (e.g. boric acid). As a result complexes between borate ions and C-2 and C-3 hydroxyl groups in the mannose units were formed. The borate ions then can be easily removed during the acidification step [4, 9, 36].

Extraction of wood hemicelluloses can also be applied using enzymes. The task of these enzymes before pulping is to extract certain amount of hemicelluloses, which otherwise is lost in the waste stream. The advantage of the enzymatic extraction over other recovery methods is mild operating conditions (room temperature, ambient pressure, and neutral pH). Other benefits are also obtained such as no damage in cellulose fibers, no chemical utilization, no excessive use of energy source, and no consequential environmental impacts. This extraction step can offer 25% hemicelluloses recovery (mostly glucomannan) from wood material. The recovered hemicelluloses can be used as a raw material of the fermentation process to produce bioethanol and chemicals such as lactic acid [30, 37].

3.3 Degradation and Hydrolysis of Hemicelluloses

Various technologies have been used for biomass hydrolysis. These include acid hydrolysis, alkaline hydrolysis, and enzymatic hydrolysis. High operating costs, negative environment impact and corrosion problems are the main drawbacks of acid hydrolysis. Enzymatic hydrolysis is considered the most promising hydrolysis technology but the using of this technique is still in lab scale [38]. Table 3.1 shows comparison of the process conditions and performance of various hydrolysis methods.

Two approaches of acid hydrolysis are commonly used: dilute acid hydrolysis and concentrated acid hydrolysis. The dilute acid process is performed at high temperature and pressure with relatively short reaction time. The lignocellulosic biomass is converted to sugars during dilute acid hydrolysis where the celluloses can be converted to glucose. Furfural can be produced by further degradation. In general, because of its branched structure and lower DP, hemicellulose is more susceptible to hydrolysis than cellulose, so that the degradation of hemicellulose-derived sugars (five carbon sugars) is more rapidly than cellulose-derived sugars (six carbon sugars). By two-stage hydrolysis process, the sugar yields can be maximized. The first stage is performed under mild operating conditions to recover the five carbon sugars, while the recovery of six carbon sugars can be optimized in the second stage [30, 38, 39].

The concentrated acid process is done in relatively mild conditions, with a much longer reaction time. Concentrated sulphuric acid is usually used to hydrolyze hemicellulosic

sugars from lignocellulosic materials and produce xylose-rich hemicelluloses [38]. The acid breaks the hydrogen bonding between cellulose chains. Complete and rapid hydrolysis of cellulose can be obtained by using warm water for cellulose dilution. However, the sugar yield is higher by concentrated acid hydrolysis [38, 39]. Partial depolymerisation of lignin-hemicellulose linkages takes place during acid hydrolysis. The hemicelluloses are broken into monosaccharides where they offer the source of carbon in fermentation media. The main content of acid hydrolysates is acetic acid (generated from acetyl groups), sugars, sugar-dehydration products (furfural or hydroxymethylfurfural), and derived compounds from soluble lignin fraction. Unfortunately, the lignin related compounds obstruct the subsequent bioconversion of the solubilized sugars into desired products, and reduce fermentation yields and rates. The use of acids or enzymes as catalysing agent in hydrolytic degradation of hemicelluloses may increase the recovery of phenols [40, 41].

The hydrolysis of biomass can also be performed using alkaline solution. Alkaline hydrolysis utilizes lower temperatures and pressures compared to other hydrolysis technologies. This technology can be carried out at ambient conditions. The cleavage reaction rate of glycosidic bonds in water-soluble carbohydrates during alkaline hydrolysis is higher than in acid hydrolysis and hydrothermal degradation. However, the yield of sugar by alkaline hydrolysis is relatively low. Organic acids are usually formed during hydrolysis; therefore, the alkali consumption by organic acid formation is the main problem of alkaline hydrolysis [30, 38, 39].

Delignification, microwave, steam explosion, and enzymatic treatment may enhance the dissolution of degraded polysaccharides. Fraction of polysaccharides can be dissolved from ground wood or pulp into neutral or slightly acidic non-boiling water. The dissolution of polysaccharides in water has great effect on the formation of intra and intermolecular interactions (hydrogen bonds) between the polysaccharides chain. Liquid water at 200-300 °C can dissolve the whole biomass hemicelluloses (90 % as monomeric sugars). Lower temperature hydrolysis can recover most of the sugars from hemicelluloses and avoid the further degradation of these sugars [9, 38].

Table 3.1: Comparisons of Different Hydrolysis Methods [38].

Hydrolysis Method	Conditions	Glucose Yield (%)	Advantages	Disadvantages
Concentrated acid	30-70 % H_2SO_4 T = 40 ºC Time = 2-6 h	90	High sugar recovery High reaction rate	Environmental and corrosion problems High cost for acid recovery
Dilute acid	< 1 % H_2SO_4 T = 215 ºC Time = 3 min	50-70	High sugar recovery High reaction rate	Environmental and corrosion problems Sugar decomposition at elevated temperature High utility cost for elevated temperature High operating cost for acid consumption
Alkaline	18 % NaOH T = 100 ºC Time = 1h	30	High reaction rate	Low sugar yield Sugar decomposition by alkali attack
Enzymatic	T = 100 ºC Time = 1.5 day	75-95	High yield of relatively pure sugar Mild operating conditions No environmental and corrosion problems	Pre-treatment of biomass required High cost of cellulose enzymes Low hydrolysis rate
Hot Compressed Water (HCW)	T = 150 -250 ºC P = 10-25 MPa Time = 20 min	< 40	No environmental and corrosion problems Low maintenance cost Relatively high reaction rate	Relatively low sugar yield

Degradation of hemicelluloses is also possible by using suitable hydrolytic enzymes. The enzymes are useful for hemicelluloses modification, and structural studies of hemicelluloses. The types of applied enzyme, the used amount of enzyme, the length of the treatment are the main parameters that affect on the degree of hydrolysis. For example, endo-mannanases enzyme is used as catalyst in AcGGM hydrolysis. The amount and type of hydrolysis product depends on the degree of substitution and distribution of the constituents of the hemicelluloses [9].

Prehydrolysis of the wood prior to kraft pulping processes is essential to produce high quality pulps. In this process, the steam is used to liberate organic acids. The high steam temperature facilitates the hydrolysation of hemicelluloses into reducing sugars. Pre-hydrolysis is usually applied with direct steam and/or hot water. Dilute sulfuric acid or hydrochloric acid is often used as the hydrolyzing agents. Organic acid typically released from wood during pre-hydrolysis [42].

Hydrothermal degradation in pure water at elevated temperature and pressure is one of the newest methods to isolate hemicelluloses from plant biomass. This method allows the gradual and temperature dependent degradation of biomass. Most of the hemicelluloses and a significant part of the lignin components are dissolved at 200ºC. Lignin compounds can be transformed into soluble compounds such as phenol around 300 °C. The degradation of cellulose part with large extent formation of monomeric carbohydrates can occur at 280°C. This method can efficiently solubilize more than 90% of the plant matter [38, 39].

In pulping industry, the release of wood components can decrease the pulp yield, contaminate process water, and increase the effluent load. Runnability problems such as deposit formation might occur in some cases. Water temperature, treatment time, pH and type and concentration of used electrolytes are the key effecting factors on wood components release. Small amount of arabinose can be released at pH around 5. On the other hand, the dissolution and dispersion of lipophilic extractives and pectins from the wood into the water can be achieved at pH around 6. The dispersion of lipophilic extractives may be decreased in the case of electrolytes presence. The treatment time is the

main important factor affecting the dissolution of carbohydrates and lignins into water. However, the lipophilic extractives dispersion does not depend on the treatment time [43].

3.4 Hemicelluloses Extraction and Recovery in Pulp and Paper Industry

Depending on the used pulping process, cellulose fibers are separated from solid wood. Complete or partial degradation of hemicelluloses and lignin occurs. Recovery of hemicelluloses in pulp and paper industry by different extraction methods shows significant potential results. Hemicelluloses are one of the dissolved organics in black liquor of kraft pulp mills. The valuable properties and functions of hemicelluloses are lost when the black liquor is incinerated [44].

In mechanical pulp and paper production, the release and accumulation of water-soluble polysaccharides in process water has undesired impact on the pulp and paper yield and on the environment [9]. The content of the dissolved or dispersed wood materials in process water of mechanical pulping is approximately 2-5 % of wood. The main dissolved components from processing of spruce wood are mainly hemicelluloses, low molar mass lignin [43].

The spruce especially Norway spruce trees are commonly used in thermo-mechanical pulping. Water soluble polysaccharides in spruce play an important role in pulp and paper manufacturing. According to Sjostrom studies [4], AcGGM was the main soluble hemicelluloses in process water of mechanical pulping of softwoods. Water extraction dissolves around 0.3 % of spruce or pine pulp in the AcGGM form at room temperature. More AcGGM with larger molar mass is dissolved when the temperature increases. The standard methods (60 ºC, mild agitation) are usually used to compare the polysaccharide dissolution from various wood species. The conditions of this method almost resemble the operating conditions in mechanical pulping. Nevertheless, treatment time extremely controls the dissolution processes. AcGGM that presents in process water of mechanical pulping can be degraded to oligosaccharides or low molar mass polysaccharides by using microwave or steam treatment. This type of treatment offers high AcGGM yield (around 80 % of the total amount in the wood). Enzymatic treatment can also enhance the dissolution of AcGGM and the obtained yield. The wood passes into different steps prior to isolation and chemical analysis of polysaccharides contents in wood. The wood must be

firstly exposed to different mechanical treatment techniques to allow smooth and complete penetration of the solvents into the cell wall. Chipping, sawing, stick preparation and grinding are usually used in mechanical disintegration. Screening is then used to offer the homogeneous woody feedstock for the further stages. High pressure (3-5 bars) and temperature (140-150ºC) are applied to disintegrate the wood structure in TMP processes. The mechanically treated woods give higher yield of polysaccharides compared to ground wood [7, 9].

The profitability of the pulp and paper industry can be improved by extracting wood components prior to pulping and converting them to valuable products especially fuel. The heating value of wood carbohydrates is relatively half that of lignin. Therefore, the extraction of hemicelluloses as oligomers, prior to pulping can be more economical use. However, understanding the kinetics of hemicellulose extraction prior to pulping is required to maintain a high pulp yield. Xylose and acetic acid are the most easily extracted components from wood. The full advantages of hemicelluloses can not be obtained during alkali pulping processes where the hemicelluloses and lignin products in the black liquor are sent to the recovery boiler [45, 46].

Number of researchers has focused to study the technical feasibility and economic profitability of production ethanol from extracted pine hemicelluloses. The integration biorefinery with kraft pulp mill for mass and energy incorporation purposes has been evaluated. Extraction of hemicelluloses before pulping the wood chips is based on balancing of the extraction operating conditions, extract yields and composition, and pulping conditions versus fiber yield and residual lignin content (kappa number). By combining the previous parameters, the raw materials requirements, energy consumption, and the size and cost of capital equipment can be estimated. The ratio of extracted hemicelluloses to other wood contents, the pulp yield from wood chips after extraction, the value of electrical power, and the cost of biofuel are the key variables to evaluate the profitability of this integration [47].

3.5 Large-Scale Recovery and Applications of Hemicelluloses

Presently, the small scale isolation of hemicelluloses has been applied for analytical purposes. The isolation of hemicelluloses for industrial applications has several difficulties since the quantity of hemicelluloses that can be produced is relatively low. Even the finding suitable enzyme obstructs the scaling up. The utilization of batch wise procedure was only suitable for production hemicelluloses in gram-scale. However, the first successful recovery in large scale for softwoods hemicelluloses was developed in 2003, where the bench scale methods were combined with inter-stage washing methods in pulp mill. Sundberg et al. [48] managed to obtain yield about 5 kg AcGGM /ton pulp. The purity of the extracted AcGGM was 95 mole %. Norway spruce TMP was used as starting material.

The process water of mechanical pulping contains significant amount of dissolved AcGGM which has 50% fraction of the dissolved matter. However, the hemicelluloses recovery from water must not disturb the main mill operations. During 2005; two TMP mill-scale trials were applied in Finland. AcGGM with 70-80 mole % purity was recovered in those trials. The apparent molar mass of isolated AcGGM was around 60 kg/mol. The yield was improved by combining membrane filtration processes especially ultrafiltration with spray drying or precipitation in ethanol. Ultrafiltration and freeze-drying was also used to recover AcGGM from process water of TMP [9, 48].

AcGGM recovery is still possible at dilute alkali solution ($\leq$ 0.05 % NaOH). The acetyl group were destroyed at high alkalinity conditions but these conditions maintain high AcGGM yield (around 70-80 %). Separation of the oligomeric substance by using gel filtration was proposed as one of AcGGM sources but nowadays it has not used any more. The presence of impurities such as lignin fragments, salts and proteins is the main problems to get pure hemicelluloses when the treatment processes that mentioned above were applied. The purity difficulties increase at large scale production so; it is difficult to obtain AcGGM without aromatic content [9, 48].

Large scale production of AcGGM for different applications has been recently studied. Nowadays, AcGGM is used in oil/water emulsion as stabilizer and in hydrophobic beverage flavours as emulsifier. Different forms of AcGGM have also been studied and used. Film form was utilized as an additive for plasticizer. AcGGM was mixed with glycerol, xylitol, or sorbitol to form cohesive transparent self-supporting films. The AcGGM with sorbitol plasticizer offers film with low permeability of oxygen at around 50% relative humidity. Unfortunately, the structural weakness is one of the drawbacks of AcGGM film, thus, other polysacchrides, alginate, carboxymethyl cellulose and konjac glucomannan have been used to improve mechanical properties of AcGGM films. Chemical modification has been applied to improve moisture sensitivity of AcGGM films. The combination of poly 2-hydroxyethyl methacrylate (PHEMA) with low molar mass spruce AcGGM from heat fractionation has showed interesting potential in hydrogels formation [9, 17].

In the past years several applications of wood derived AcGGM came into sight in textile industry, and medical fields. Native or modified AcGGM were applied through sorption to modify the properties of products that based on celluloses surface as in papers, antibacterial bandage and abrasion-resistant clothing. Other promising applications such as barriers against water vapors were also evaluated. It can also be used as fat barriers in food pack [9, 49].

The extraction and purification methods have the major effect on the yield and structure of the recovered hemicelluloses. Large scale ultrafiltration was promising to recover dissolved polysaccharides from process water of mechanical pulping of Norway spruce wood. The biological activity and physico-chemical properties of the wood hemicelluloses show motivating potential to find large scale novel applications in various industrial processes [9].

3.6 Precipitation and Purification of Hemicelluloses

Barium hydroxide is often used to enhance the selectivity precipitation of GGM in alkaline extraction. This agent forms insoluble complexes with C-2 and C-3 hydroxyl groups in the mannose units. Fehling's solution and alkaline copper salts can also be used as precipitation agent. Other polysaccharides can be selectivity precipitated from the solution by using other agents. So, cetyl trimethyl ammonium hydroxide or cetyl pyridinium chloride has been applied for precipitation of acidic polysaccharides. Miscible organic solvents especially ethanol can also neutralise and precipitate the soluble polysaccharides. While most of soluble polysaccharides precipitate using ethanol (ethanol to water ratio is around 4:1), the oligomeric and monomeric carbohydrates remained in the water solution. The purity of precipitated AcGGM can increase using sequence of precipitation in ethanol. Unfortunately, some problems such as co-precipitation of other dissolved polysaccharides can take place in some cases [9].

Various fractionation columns with different characteristics such as hydrophobic, cationic and anionic columns have been mainly used to fractionate softwoods polysaccharides. Chromatographic methods give highly efficient removal of non-polysaccharide substances such as lignin and lipophilic extractives. These methods show lower efficiency in separation of pure fraction of polysaccharides. The scaling up of chromatographic columns offers successfully results when they are applied for removal of extractives and lignin impurities while the using of these columns in industrial scale separation of different polysaccharides is difficult. Membrane separation processes especially micro or ultrafiltration have also been used to remove impurities from AcGGM [9].

3.7 Pressurized Hot Water Extraction (PHWE)

3.7.1 Basic Principles of Pressurized Hot Water Extraction

In the extraction process the target compounds have to dissolve in the extraction solvent. The solvent molecules form layer around solute molecules, where new type of interaction between solvent and solute molecules are established. The solubility (δ), polarity (α), dipole moment (μ), formation of hydrogen bonds and the sizes of the solute and solvent molecules are the main parameters having significant role in the solvation processes. In

water solvent processes, such as PHWE, the induction, dispersion, and ionic interaction are the major intermolecular interaction between water and solutes. The dipole-dipole interaction and hydrogen bonds are also formed.

Hot water extraction at atmospheric pressure with temperature ranges from 50-100 ºC has firstly been used to extract organics from solid materials. In these conditions, the polar and water-soluble compounds are usually extracted. In 1994 the utilization of hot water to extract non-polar organic compounds from solid matrices was proposed. This type of extraction based on the special solvent properties of water, i.e. at higher temperature, the polar behavior of water will decrease. Various terms such as sub-critical water extraction, superheated water extraction, extraction using hot compressed water, and pressurized hot water extraction have been used to describe this extraction method. Nowadays, most of pressurized hot water extraction applications involve the pretreatment of solid materials. Extraction of aromatic compounds from herbs and other plants and organics pollutants from soil are the main areas of PHWE applications [50, 51].

Low cost, polarity, and non toxicity are the important characteristics of water as the extraction solvent. Temperature is used to merely modify the dissolving power (polarity) of water. The key factor that clarifies the polarity effect and interaction between solute and solvent is dielectric constant (ε), this factor decreases with increasing temperature. A solvent with high dielectric constant is preferable to solvate highly polar and ionic compounds, while a solvent with low dielectric constant is used to solvate low polarity compounds. The dielectric constants and densities of gaseous and liquid water are equal at critical pressure and temperature of water. At sub-critical conditions, non-polar gases and organic compounds are highly soluble in water. When the temperature increases, the hydrogen bonding between water molecules decreases and that causes decline in the solubility of inorganic (ionic) compounds in water. The dielectric constant of organic solvents often drops from 80 at room temperature to 10 at above 300ºC [50].

The operating temperature and pressure have the main effect on PHWE process selectivity. The trapping methods of target compound also have influence on selectivity. The diffusivity (D) and thermodynamic partitioning (K_D) are the main parameters that describe desorption and elution of target compound from solid matrices. The extraction

rates increase with hot water flow rate. In some cases the high selectivity extraction from natural products occurs, when the target compounds selectively react with water during extraction (e.g. hydrolysis) [50].

Self - built PHWE equipments are usually created. Modification from other related extraction equipment such as supercritical fluid extraction (SFE) equipments, and pressurized liquid extraction equipments are usually used. The PHWE equipments have to tolerate high temperatures sometimes over 300ºC. Constant dynamic mode of water is often considered in design of PHWE equipments. The main components of the equipments are high pressure water pumps, stainless steel extraction vessels, heaters for the extraction vessels, cooling capillaries, pressure restrictors and collection systems [50, 51, 52].

Various trapping systems are often used in PHWE. Micro-porous hydrophobic membranes are frequently used when the target compounds are trapped into organic solvent. Solid-phase micro-extraction (SPME) is also used as a trapping system in PHWE. Utilization of solid-phase traps offers additional selectivity. Several online alternative chromatographic techniques are successfully connected with PHWE. This coupling can be with gas chromatography (GC), liquid chromatography (LC) and superheated water chromatography (SWC). Special solid phase sorbents or trapping solvents can also be used to collect the extracts and enhance the selectivity of target compounds. Polar modifier such as ethanol can be added to enhance the extraction processes. Other modifier such as sodium dodecyl sulfate (SDS) and acidic water can be used, but the corrosion problems may occur when acidic water is used as extractant. [50, 51, 52, 53].

3.7.2 Parameters Affecting the Pressurized Hot Water Extraction (PHWE)

In PHWE processes temperature, pressure, extraction time and solvent characteristics are the main parameters to be considered. Other parameters such as flow rate, type of extraction vessel, solid matrices, target compound and use of modifiers and additives are also affecting. Efficiency of PHWE depends on the dynamic mode of liquid water flow through the solid phase [50,51].

3.7.2.1 Temperature

Temperature is the main parameter that has the great effect on the physicochemical properties of water and the compounds to be extracted, and it also influences on the efficiency, selectivity and extraction rate in PHWE. Several physical advantages such as fast diffusion, low viscosity, and low surface tension are obtained, when the water is pressurized. These advantages are also achieved in sub-critical fluids (SCFs). Several favourable thermal effects such as increasing the vapor pressure and accelerating thermal desorption of the extracted compounds are obtained in PHWE. These effects enhance the efficiency of extraction by pressurized hot water. At high temperatures, the attractive forces of water will be closer to the forces of non-polar compounds, thus the solvent properties of water are significantly altered and the solubility behavior of less polar compounds in water noticeably enhances. The ionic, hydrogen bond, and dipole-dipole interactions between water molecules decrease at the temperature between 100-200 ºC. However, the water will still have degree of hydrogen bonds at supercritical conditions [50, 51].

In general, when the temperature increases; the degradation of the compounds such as hydrolysis increases. Commonly the organic compounds are rapidly decomposed at high temperatures. Structural changes in matrices with high organic content (e.g., plants, food, synthetic polymers, and plastics) may also occur at high temperature conditions, which may influence the selectivity and performance of extraction process. While the solubility of organic compounds rapidly increases with temperature, the inorganic compounds solubility decreases. So, the operating extraction temperature can be used to achieve selective extraction of different polar compounds. By increasing temperature the class selective extraction of thermally stable compounds can be carried out. The degradation of thermo-labile compounds may also occur [50, 51].

According to compounds polarity the extraction of polar compounds is generally efficient at relatively lower temperatures than non-polar ones. While the recommended temperatures of polar compounds extraction are from 100-150ºC, the preferable range of extraction temperatures of moderate and low polar compounds is from 200-300 ºC.

Relatively large amounts of non polar extracts are obtained at higher temperature. So, the extraction of non-polar compounds at high temperature is recommended [50, 51].

For non polar compounds that are non-soluble in water at ambient conditions, water can be a good extraction medium at high temperature. Sufficient extraction of many low polarity compounds can be accomplished at temperatures much lower than critical temperatures. Quantitative water extractions at temperature lower than the critical temperature of water can be applied for removal of small amounts of non-polar organics even the maximum solubility conditions are not available [50,51].

Several factors such as the solvent strength of water and the degree of the thermal effects that influence extraction efficiency can be adjusted with the temperature. These factors demonstrate the dependency of the extraction selectivity on the solute polarity. Although the running of PHWE at higher temperatures conditions is preferable; some negative effects such as corrosion in extraction instrument, degradation and decomposition of target compounds and possible side reactions may occur. Leaking and extraction of impurities are also possibly occurring when extraction temperatures are very high [50, 51].

3.7.2.2 Pressure

The effect of pressure is lower than temperature effect on solvent properties of water. In general, when the pressure increases, a slightly increase in permittivity can be noticed. This increase may impede the extraction of the non -polar compounds. However, pressure has only minor effects of the solvent strength of liquid water and relative permittivity. In the practical extraction processes, the liquid phase of water is kept at various extraction temperatures by adjusting the operating pressures. Higher pressures improve the accessing of the water through the solid matrix. High pressure compensates the back-pressure generated by the solid materials and instrumentation. The determination of lowest operating temperatures depend on the pressure needed to pump the water through the PHWE system [50, 51].

Steam extraction of non-polar and slightly polar compounds is more efficient and commonly used than liquid water extraction at the same temperature. The pressure must be monitored to ensure the water to be in gas phase. Homogeneous flow of steam is

attained at lower pressure. However, the temperature is restricted to around 150ºC in steam extraction, when pressure (5-10 bars) is needed to satisfy efficient and constant flow through the solid sample. Low relative permittivity of steam and better repeatability are the main factors that enhance the steam extraction efficiency of non-polar compounds. The uniformity of steam flow offers another advantage for this extraction [50, 51].

3.7.2.3 Extraction Time, Flow Rate and Extraction Vessel

Extraction time, flow rate, the size and shape of extraction vessel are also important factors for optimization of extraction operations. The extraction time significantly depends on the operating temperature and the nature of the solvent and solute. The increasing temperature decreases the time required for quantitative extraction. Long extraction time is required if the extraction temperature is too low [50, 51].

The partition-equilibrium constant and the solubility of compounds are the major parameters that have to be considered to improve efficiency of static extraction mode. Conversely, the complete equilibrium is reached as fresh solvent is continuously pumped through the process. The time required for complete extraction can be shortened by installation of a static extraction step before dynamic extraction. Increasing the flow rate enhances the extraction efficiency because the total volume of solvent in the process is increased. In addition, physical transfer of solute to solvent is also improved at higher flow rate consequently the higher recovery of the solute [50, 51].

In general, both of the geometry of the extraction vessel and the direction of flow have noticeable effect on the recovery. The relatively short and wide vessel gives higher average recoveries than long vessels in extraction with steam. On the other hand, long vessels with narrow inside diameter offer higher recovery than short and wide vessels when the water in liquid phase is used as a solvent in the extraction operations. Long path gives easily and efficient flow of water through the extraction operations. The upwards water flow in the vessel (fully loaded) is useful to effective remove air present in the tubing and in the extraction vessel especially at the beginning of the extraction. In not fully packed vessel, the effects of vessel geometry and flow conditions have a greater importance. The compound properties affect on the required flow rate in the recovery process [50, 51].

3.7.3 Extraction and Separation of Hemicelluloses by Hot Water

The consumption of large amounts of organic hazardous solvents in chemical separation processes especially in the solvent extraction and the increasing costs of organics solvent disposal have grown the demand to seek more environmentally friendly solvents in chemical process applications. The extraction of low polarity compounds by water is possible at temperatures below critical point if they have sufficient solubility at those conditions. Dielectric constants and densities for gaseous and liquid water are the same at these conditions (374 ºC and 221 bars). Thus, adequate recovery of organics with different polarity from solid matrices can be achieved by using water in liquid or vapour form at temperatures from 200-300 ºC. The extraction technology that base on modification of the properties of water by increasing the temperature up to 374 °C and maintaining the pressure high enough to keep water in the liquid state is called pressurized low-polarity water (PLPW) extraction or sub-critical water extraction. The advantages of this extraction process over than other conventional extraction techniques are higher selectivity, cleanliness and saving on solvent and energy consumption [50, 51].

Significant researches and developments based on using hot-compressed water for biomass hydrolysis have been done in the past few decades. Liquid water at high temperature and pressure can be used to fractionate biomass into its components. The use of acids especially acetic acid as hydrolysis catalyst can enhance the water ionization at the fractionation temperatures (180-240 ºC). The depolymerisation of hemicelluloses can occur at these temperatures. Hot water extraction (prehydrolysis) for one hour at 180 ºC has been applied for selective removal of hemicellulose from pine woods before chemical pulping processes. Mok and Antal [54] achieved complete removal of the hemicelluloses from biomass and herbaceous materials without high degradation by using around 15 minutes hot liquid water extraction at 200-230 ºC. Partial depolymerization and solubilization of the lignin can take place during this extraction. However, utilization of hot water alone can not satisfy complete delignification. The dissolution of cellulose can only be achieved at higher water temperatures. The maximum solubilization of the cellulose (recovered as glucan) at 200-230 °C from biomass was around 22 %. The biomass fractionation is only possible by water steam at this temperature range. The water steam can dissolve the hemicelluloses but it can not satisfy complete removal of lignin.

Bobleter [55] pioneered hot-water pre-treatment of biomasses. In his work, higher hemicelluloses recovery and greater lignin removal could be obtained by passing hot water continuously through a stationary biomass. Generally, significant increase of hot water flow rate enhances the hemicelluloses removal.

Conversion of lignocellulosic biomasses to ethanol consists of a four operations: biomass pretreatment, hydrolysis, fermentation and product separation and purification. Wyman et al. [56] evaluated the performance of different pretreatment methods of corn stover using water, acids, lime or ammonia. Pretreatment using hot liquid water can be a promising process to improve cellulose digestibility, sugar extraction, and pentosan recovery. In this type of pretreatment, the hemi-acetal linkages of hemicellulose are cleaved, O-acetyl and other acid moieties are liberated from hemicelluloses. This allows to form and release acetic and uronic acids. However, these acids are useful to catalyze removal of oligosaccharides from hemicellulose. The optimization of pre-treatment processes is usually based on highest overall sugar yield with minimum degradation of the carbohydrate component.

Van Heiningen et al. [57] studied the influence of the hot water extraction operation conditions such as temperature, time and chip dimensions on the extraction yield of hemicelluloses from mixed southern hardwood. They used (modified) Dionex ASE-100 (Accelerated Solvent Extraction Equipment) when the high pressures were required. The composition of the extract hemicelluloses was determined by HPAEC analysis. The molar mass distribution of hemicelluloses in the extract was determined by using gel permeation chromatography (GPC).

Jollez et al. [58] obtained around 50 % solubilization of the sugarcane bagasse polysaccharides by hot water. The carbohydrate degradation by hot water fractionation is usually lower than by steam. Hot liquid water fractionation usually satisfies higher hemicelluloses recovery. Allen et al. [59] employed aqueous fractionation device (Figure 3.1) to solubilize 54 % hemicelluloses at 215 °C using hot liquid water at 5% solids loading. The process recovery indicated that the large pretreated oligomeric carbohydrates can be efficiently recovered more than pretreated monomeric xylose under similar conditions. However, monosaccharides are usually maintained in the form of oligomers.

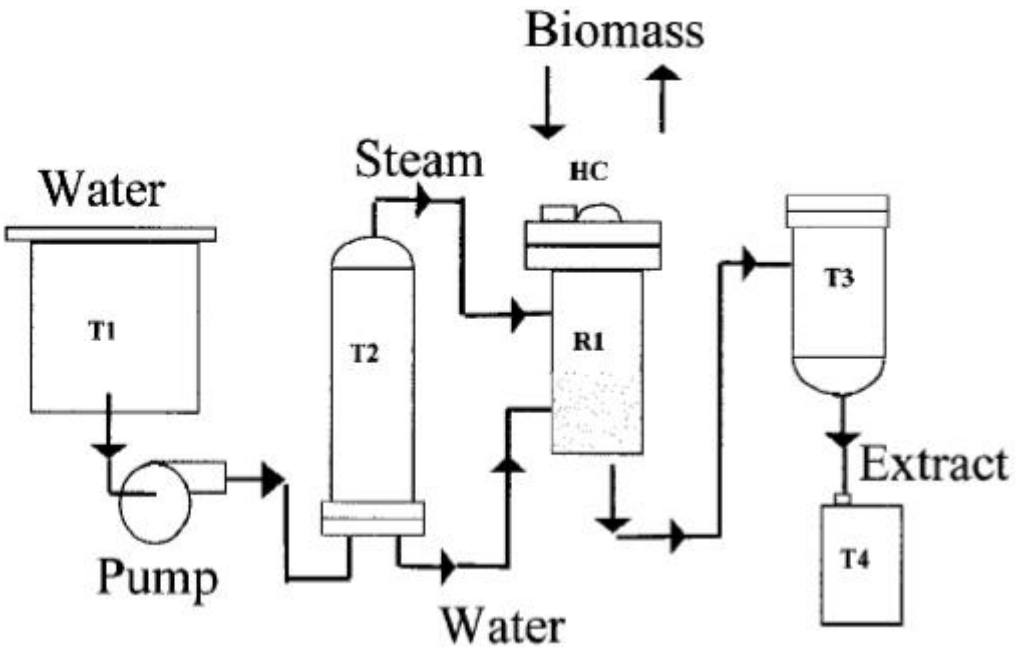


Figure 3.1: Schematic Dagram of the Aqueous Fractionation Device, showing the (T1) feed water tank, (T2) boiler, (R1) reactor with (HC) hinged closure, (T3) product tank, and (T4) product reservoir [59]

Lundqvist et al. [60] studied the amount of mannan that can be yielded by impregnation of spruce chips in different media prior to the microwave heat-fractionation of the hemicelluloses. The goal of their study was to find the optimum conditions to obtain high hemicelluloses yield with high molar mass from water extraction of spruce chips GGM using microwave heat-fractionation. Their work focused on the effect of temperature, residence time and pH of heat-fractionation, on the weight-average molar mass of extracted hemicelluloses, the extraction yield (% oligo- and polysaccharides), and composition of the extracted galactoglucomannan (GGM). However, the highest extraction yield of mannan was 78 % (based on the amount in the raw material) using water impregnated spruce chips. The molar mass of the extracted mannan was 3800 g/mol. The heat-fractionation was performed at the operating temperature of 190º C and 5 min residence time. While the pH of the extraction water was 5.3 after impregnation, it was 3.4 after heat fractionation.

Liquid hot water pretreatment has the potential to improve sugar extraction from biomass. The obtained pre-hydrolyzates do not impede the fermentation of sugar. The effective pretreatment requires optimal process conditions to improve overall sugar yield and minimize the carbohydrate degradation. The effect of temperature, residence time, solid concentration and overpressure applied in the pretreatment reactor on liquid hot water pretreatment of wheat straw was studied by Pe´rez et al. [61]. The evaluation of this pretreatment process efficiency was based on the composition of the solid and liquid fractions in the pretreated material, and degradation ability of the solid fraction in enzymatic hydrolysis.Their study showed that the temperature and time have a significant effect on the pretreatment efficiency. The effect of pretreatment time on hemicellulose-derived sugar recovery depended on temperature. The maximum hemicelluloses recovery they got was (53% of content in raw material). The increase in pretreatment temperature and time enhanced yield of enzymatic hydrolysis. The greatest yield they obtained was 96 % at 200 ºC and 40 min. Their study proved that the liquid hot water pretreatment can be an effective process to enhance the potential of wheat straw as a raw material for ethanol production.

Hasegawa et al. [62] developed pretreatment method for complete separation of hemicelluloses, cellulose, and lignin from biomass. Their method was performed in two approaches. The first approach was done by combining a conventional hot water treatment with acetone water mixture extraction using a batch or a continuous flow reactor. The other approach was done in one water/acetone extraction step. While the optimum temperature for hot water treatment was 180°C, the optimum temperature for a water/acetone extraction (two steps) was 230 °C and 200 °C for one-step water/acetone extraction. The optimum acetone concentration was 50% for the water/acetone extractions. In the two extraction steps, hemicelluloses were recovered as polysaccharides by hot water extraction and cross-linked cellulose and lower molar mass solubilized lignin were recovered by water/acetone extraction. In a one-step extraction hemicelluloses and lignin were recovered together.

Palm and Zacchi [63] tried to isolate hemicellulosic oligomers from spruce wood using steam treatment. The separation of oligmeric compounds from the liquid fraction was performed using gel filtration. Removal of lignin or lignin complexes from the oligomers

was also investigated. The steam treatment of spruce was successfully done at 200 ºC for 2 min to isolate oligomers from other low molar mass compounds. By this treatment, around 6 g oligomers /100 g dry wood was obtained. The results of this study showed that gel filtration can be successfully performed to obtain oligomeric materials free from monomeric sugars. Furthermore, partial removal of lignin compounds from oligomeric fractions can also be achieved using gel filtration.

Karlsson et al. [64] aimed in their study to obtain high yield of hetero-polysaccharide fraction using hydrolytic pre-treatment for wood chips. The pre-treatment step of wood chips was followed by Extraction at room temperature. Acetic acid, sulphur dioxide and water at high temperature were used as pre-treatment solution. Extraction yield, chemical composition and molar mass of extracted components were used to characterize the isolated fraction. In their study, isolation of high yield heteropolysaccharide fraction with high purity and molar masses from birch wood using acid catalyzed pre-hydrolysis (prior to kraft delignification) was optimized. The composition and properties of the pre-hydrolysis solution (water, dilute acetic acid, dilute sulphur dioxide) and the processing conditions (pH, temperature and time) were the major affecting factor on the extracted materials yield. The amount of extracted material using water, acetic acid and sulphur dioxide were 3.2, 8.0, 8.3 w/w % respectively.

Hartonen et al. [65] investigated the optimal conditions (time, pressure, temperature) of pressurized hot water extraction to recover flavonoids and other phenolic compounds from aspen knotwood. They compared PHWE with other techniques (Soxhlet, reflux and ultrasonic extraction in organic solvent). They found, PHWE techniques offers fast, environmentally friendly, cheap, and effective alternative to isolate valuable bio-functional compounds from solid samples such as wood. Buranov and Mazza [66] have evaluated the efficiency of the pressurized low polarity water (PLPW) extraction process to remove hemicelluloses from flax shives. A PLPW extraction was operated in two steps, the first one with water and the other with aqueous ammonia. In this process, all of the hemicelluloses xylan was removed during the first stage with water and the lignin was removed during the second stage. They found that the PLPW extraction process of flax shives efficiently removed hemicelluloses. The removal of hemicelluloses was 85% using

water. The required amount of water to extract hemicelluloses from flax shives was around 8 mL/g flax shives.

Pretreatment of biomass with compressed hot water or steam is called auto- hydrolysis. Operation without chemicals makes the process attractive. Accelerating of hemicelluloses solubilization and increasing the hemicellulose yields can be achieved by passing compressed hot water through stationary bed of biomass [55]. Antal et al. [54] achieved complete hemicelluloses removal from different biomass species using flow-through pretreatment. Compressed hot water flow rate can enhance the removal of hemicelluloses and lignin. However, very dilute sulphuric acid at elevated temperatures can be used in flow-through approach. Fluid velocity and residence time are the main parameters that control hemicellulose hydrolysis. Unfortunately, large consumption of water can be one of the flow-through system drawbacks. A new partial flow pretreatment approach was suggested to avoid high water consumption. The use of partial flow pretreatment gives lower water consumption and maintain relatively high hemicellulose sugar yields, lignin removal, and cellulose digestibility [67, 68,69].

Hot compressed water shows unique properties in various biomass utilization purposes including hydrothermal degradation of lignocellulosic biomass for bio-fuel production. The decomposition mechanisms of hemicelluloses using compressed hot water are similar for different carbon sugar. Lignocellulosic materials pretreatment strategies focus on hemicellulose recovery. Hemicellulose-derived sugar can be possibly recovered using large amount of water. Dilute sugar solution containing water soluble sugar compounds was usually obtained. Generally, the amount of wood-derived water-soluble hemicelluloses is typically from 30 to 60 g /L; in contrast, the industrial fermentations require sugar concentrations on the order of 100–300 g /L [69, 70, 71].

Hot compressed water was used to study the decomposition behaviors of bamboo, chinquapin (hardwood), and Japan cedar (softwood). Some of lignin and most of hemicelluloses were solubilized during 20 minutes of hot compressed water operation at temperature range between 180°C-285°C. The hemicelluloses started to decompose at 180 °C. Because the decomposition of lignins occurs at lower temperatures, the decomposed lignins were flowing out with the decomposed products of hemicelluloses. Therefore, it is

important to develop processes to separate the lignin components from hemicelluloses and to improve the sugar recovery. Hot compressed water pretreatment can be novel process for separating part of the hemicellulosic components of wood prior to further processing [72].

A complicated reaction pathway of hydrothermal reaction is the main difficulty in optimization of hot compressed water (HCW) biomass hydrolysis. The optimization of biomass decomposition can be achieved using two HCW steps pretreatment. By this approach, the yield of water soluble sugars can be enhanced, and the side reactions of hemicelluloses can be avoided. Continuous flow type reactors can be used to satisfy higher sugar recovery. It was reported that, around 100% of the hemicellulose can be solubilized at 180–200 °C, of which 80–90% is recoverable as monomeric sugars [38, 54].

Amidon et al. [46] succeeded to decrease alkaline pulping reaction time by 20-87.5 % using hot water pre-extraction (HWP-E) of wood. The efficiency of this pretreatment depends on cooking parameters and severity of HWP-E. The chemical and physical properties of the wood components can be changed using hot water pretreatment. The alkaline pulping parameters can be also changed. The delignification of the pretreated wood can be simple. Removal around 5 % wood chips hemicelluloses using milder extraction conditions is ideal to achieve competitive conventional pulping yield. This fraction can be good enough to satisfy shorter cooking times, higher yields and better bleaching ability.

Pretreatment of plant materials can also be done using liquid hot water with controlling pH. Maximum hemicellulose solubilization as liquid soluble oligosaccharides with minimum monomeric sugars formation can be achieved by controlling pH in liquid hot water pretreatment process. The optimization conditions for this process were 190 ºC for 15 min at pH between 5 and 7 [73].

4. ANALYSIS AND CHARACTERIZATION OF WOOD HEMICELLULOSES

Alkaline extraction is the standard method to separate hemicelluloses from its sources for analysis purposes. Previously, classical wet chemical methods were used to determine the wood components quantitatively. Nowadays, new analytical methods based on chromatography or spectroscopy or combination of the two can provide the needed molecular level information about the wood components [7].

Several analytical methods are used to investigate the structure of polysaccharides. Hydrolysis, partial hydrolysis, oxidation, and permethylation were mainly applied to treat polysaccharides before analysis. Various fractionation and purification methods such as precipitation, complex formation, and paper and thin-layer chromatography are also frequently used [7].

4.1 Classical Standard Methods

Various gravimetric methods based on the solubility of the wood components in alkali solution have been used to determine the total amounts of hemicelluloses and degraded cellulose in pulp samples. A sodium hydroxide solution at 25 ºC is usually used to extract hemicelluloses. The soluble hemicelluloses are determined by oxidation with potassium dichromate. A corresponding method with slightly different conditions has been described to dissolve carbohydrates. In this method both hemicelluloses and degraded cellulose can be dissolved using 10 % sodium hydroxide solution, whereas hemicelluloses can be only dissolved using 18 % solution. The differences between two solubilities can be used to estimate the degraded cellulose content. [7].

Classical wet chemical methods can be used for quantitative determination the hemicellulosic wood components. Preparative isolation of the group of interest before analysis is required to perform detailed structural analysis. However, it is very time consuming to isolate and purify the required component before analysis using these methods. Therefore, there has been a large interest to develop applicable analytical method without using tedious pretreatment procedures. Nowadays, the development of new

chromatographic and spectrometric methods offer direct, faster analysis of wood components and functional groups in wood and pulp samples [7].

4.2 Chromatographic Techniques

Chromatographic techniques are the most important tools for the separation and analysis different components in wood. Large scale preparative separation can be performed by chromatographic techniques. This separation is used for further analysis by other techniques. Both polymers and low molar mass components can be separated by chromatography. The separation of the individual components can be complete separation, whereas polymer separation usually occurs in groups. The two main chromatography instruments that are usually used for wood components analysis are liquid chromatography (LC) and gas chromatography (GC) [7].

Size exclusion chromatography, also called gel permeation chromatography, is one of the important forms of high performance liquid chromatography (HPSEC). Micro-porous particles columns such as synthetic cross linked polystyrene resins are usually used in HPSEC. The separation principle is based on the hydrodynamic volume differences between different molar mass molecules. Polymers with known properties and similar structure are used for calibration. HPSEC can give the molar mass distribution of dissolved lignin and hemicelluloses. Recently, HPSEC showed valuable results for extractives analysis. Previously, several physical methods such as osmotic pressure or ultracentrifugation have been used to determine the molar mass of the components separated by HPSEC. Other chemical methods based on reduction reactions of the end groups have also been utilized. Currently, refractive indexes, UV, laser light-scattering or matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) is often used to determine the molar mass of poly or oligosaccharides separated by HPSEC. However, a comparison between different analysis results is the main difficulty when different analytical techniques are applied [7].

Three different HPLC systems have been used for wood sugar analysis. The derivatization of the sugars is not necessary in HPLC analysis. Pulsed Amperometry Detectors (PAD) can be used for sensitive and specific detection of carbohydrates. Use of HPAEC-PAD system (High Performance Anion Exchange Chromatography with Pulsed Amperometric

Detection) gives good baseline resolution and perfect detection of the main neutral wood sugars [7].

One of the newest forms of liquid chromatography is capillary electrophoresis (CE). This method uses fused silica columns, where the electrical field across the column is the main driving force. The separation is based on charge to size ratios differences between various molecules. The analysis of lignin and carbohydrates has been performed by CE. Different detectors are used to detect eluting component from liquid chromatography. Pulsed ampero-metric detectors are one of UV or refractive index (RI) detectors that provide highly sensitive detection of mono and oligosaccharides. High performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) is also an important technique for sugars analysis in wood and pulp hydrolysates [7].

Conventionally the analysis of hydrolysed wood monosaccharides has been done by paper chromatography. Nowadays, gas chromatography is efficiently used. Direct combination of gas chromatography (GC) with pyrolysis expands the application of this technique to solid samples and polymers. Pyrolysis - gas chromatography-mass spectrometers (Py-GC-MS) has been used for characterization and quantification of lignin and carbohydrates in wood pulps. GC is now used in analysis of lignin degradation products, and various extractives. GC is the major method for the analysis of the pulp and paper effluent components [7].

4.2.1 Hydrolysis and Chromatographic Techniques

Total acid hydrolysis and chromatographic analysis of the hydrolysed monosaccharide can be used to determine the content and sugar composition of cellulose and hemicelluloses in wood. The standard hydrolysis technique contains two steps using 72% and 3% sulphuric acid. The use of trifluoroacetic acid instead of sulpheric acid can cause less degradation of monosaccharides.

Enzymatic hydrolysis is the gentle method in the case of dissolved polysaccharides. It is promising technique to hydrolyze polysaccharides. The hydrolysis time of this analysis is 48 h and the temperature and pH is 40 ºC and 5, respectively [8]. The enzymatic hydrolysis is useful to give detailed structural analysis of polysaccharides by providing

selective cleavage of specific glycosidic linkages. However, good specification requires pure enzymes. Utilization of enzymatic hydrolysis with linkage and sequence analysis is facilitated the analysis of linkages between different polysaccharides. Nevertheless, combination of different analytical techniques is considered to be the best approach to get complete information about structural characterization of different polysaccharides [9].

GC and HPLC are efficiently performed in analysis of hydrolysed sugars. The utilization of GC standard method involves reduction of the sugars, followed by acetylation with acetic acid anhydride and sulphuric acid. The acetylated sugars are extracted into dichloromethane. These sugars can be analysed by packed GC column. Packed columns are replaced by capillary GC columns for wood and pulp analysis. These columns provide significantly better peak resolution that improves the sensitivity and the quantity determination of small sugar components. The analysis of hydrolyzates of the wood sugars in mixtures can be done using capillary columns without reduction. Modern chromatographic systems can easily handle very complex wood components. The coupling of silylation (the simplest derivatization procedure) and GC has been successfully applied in the analysis of very complex hydrolysates containing various glycose and hemicellulose sugars [7].

4.2.2 Methanolysis and Gas Chromatography

Methanolysis has great advantage over hydrolysis where the degradation of released monosaccharides is lower. This method has been successfully used for analysis of the hemicelluloses. Acid methanolysis can be directly performed to give quantitative determination for dry wood hemicelluloses. The hemicelluloses and pectins are cleaved to monosaccharides using this method. Precipitated glucomannans by deacetylation can not be completely accounted in the analysis.

The methanolysis-GC gives convenient alternative method in analysis of wood hemicelluloses with low sugar losses by degradation. In this system, the interpretation of the obtained monosaccharide composition into different hemicelluloses types must be based on knowledge or estimation of various hemicelluloses types and their approximate monomer composition [7, 74]

4.3 Spectrometric Techniques

UV spectrometry is the most used technique to determine the lignin contents. Colorimetric methods followed by spectrometric techniques can be used to determine hemicelluloses and pectins content.

Near Infrared (NIR) spectrometry is a simple and rapid technique that operates in the wave length range of 800-2400 nm to give general characterization of wood and pulp. Raman spectrometry is one of spectroscopic techniques that use scattered light to pass through the sample molecule. Analysis of lignin in wood pulp is the most important applications of Raman spectroscopy. Insensitivity of Raman spectroscopy for water is one of its advantages. However, this spectroscopy is more sensitive to extractives, lignin, and carbon-hydrogen bonds of the polysaccharides [7].

Nuclear Magnetic Resonance (NMR) spectroscopy has also been used to analyze lignin compounds. This spectroscopy can provide valuable structural information when it is used for the analysis of lignins and hemicelluloses. Using of NMR requires dissolved samples in relatively high concentration to get high resolution [7].

Solid-state C NMR was developed to allow direct in-situ analysis of wood and pulp samples. This spectroscopy type can give very useful information about the chemical and physico-chemical properties of wood components. In spite of the unique structural information of wood components able to be obtained by NMR, limited industrial applications for this spectroscopy are existed for pulp and wood analysis. This is mainly due to the high cost of the equipment, high experience requirements, and lack of online connections [7].

Matrix Assisted Laser Desorption / Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) is a mass analysis technique that is suitable for detecting high molar mass compounds. It has been extensively applied for polysaccharides such as xylan analysis [7].

4.4 Structural Determination of Wood Hemicelluloses

Obtaining the complete polysaccharides structure requires determination of many molecular parameters such as the ring structure, individual sugar unit configuration, sugar unit sequences in the main and side chains and glycosidic bonds positions and configuration between the sugar units. Detailed structure determination requires preparative isolation of the polysaccharides in pure form. Because this is laborious, it is only used in basic studies on wood. NMR spectroscopy is the most important tool that is used for structural analysis of wood [7, 29].

Methylation analysis can be the most convenient method for determination the position of glycosidic linkage between the sugar units. GC-MS analysis can provide information of which hydroxyl groups had been involved in acetylated linkages. Clearing of perm-ethylated polysaccharides to monomers can be done by methanolysis. Capillary GC can give good resolution in analyzing complex mixtures and even mixtures of hemicelluloses or mixture of degraded hemicelluloses (monomers) [7].

Selective enzymatic hydrolysis is the most common method to determine the sugar sequences in the chain. By applying specific exo-hydrolases, the analysis of wood polysaccharides components can be performed. The analysis of the resulting mono-and oligosaccharides can be done by HPLC. Determination of the uronic acids and acidic oligosaccharides obtained by enzymatic hydrolysis of wood can be achieved by capillary electrophoresis [7].

Fast Atom Bombardment-MS is a valuable technique can be used for analysis of oligosaccharides obtained by partial hydrolysis of polysaccharides. More information about sugar sequencing can be obtained by forming series of ionic fragments through cleavage of glycosidic bonds. Matrix -assisted laser desorption /ionization (MALDI) in combination with Fourier transform mass spectrometry is a new technique for obtaining information about oligosaccharides sequences and linkages [7].

4.5 Analysis of Process Waters and Effluents Containing Hemicelluloses

The process water of pulp and paper mills usually contains dissolved and dispersed wood material with concentration around 30-60 kg/t. These materials are usually composed of hemicelluloses, pectin, lignin, lignans, and wood resin. Hemicelluloses and theirs degradation products are one of the main components in kraft cooking liquor. Hydroxyl carboxylic acids are the main degradation products of hemicelluloses in these liquors. The isolation of hemicelluloses from process waters can be done using ethanol precipitation. Hemicelluloses can be selectively precipitated using 1, 4-dioxane and acetic acid. The purification of the isolated hemicelluloses can be performed using dialysis. Acid precipitation can be suitable for lignin removal [7].

Various gravimetric methods have been used to fractionate polysaccharides into water soluble hemicellulosic, and cellulose fractions. Appropriate preparative isolation procedures are needed to give detailed structural characterization for different hemicelluloses types. Ion exchange resins can be used for anionic hemicelluloses isolation. However, characterization and analysis of hemicelluloses in lignocellulosic material typically depend on the selected fractionation techniques [7, 75].

Gas chromatography and spectrophotometric methods are usually used to determine the sugar and uronic acid compositions of hemicellulosic, and cellulose fraction. Convenient detailed quantitative determination of different dissolved and colloidal wood components in paper mill process streams and effluents can be obtained by using practical integrated analytical system. In this system, the amount and composition of hemicelluloses is determined by GC after cleavage to monomers by methanolysis. GC analysis of freeze-dried samples can be directly used to determine content of simple saccharides such as mono-and disaccharide. Presence of dissolved lignin and lignin –like substances in water can be determined using UV absorption spectrophotometer at wave length around 280 nm. The analysis of such samples requires less than 10 mL volume [7, 75].

Low molar mass degradation products derived from hemicelluloses such as aliphatic acids can be identified using various extraction techniques such as anionic exchange or solvent extraction. The analysis of the extracted compounds can be done by capillary GC and GC-

MS using different derivatization techniques. Ion chromatography has been used to determine formic and acetic acids. The detailed analysis of hydroxyl carboxylic acids can be performed in two steps, the first one is extraction using cationic exchange resin, and the second is analysis using GC and GC-MS [7].

The average molar mass of hemicellulosic fractions in process water can be estimated using gel permeation chromatography. Size exclusion chromatography (SEC) in buffered water systems can provide valuable information about molar mass of polysaccharides. Characterization and estimation of the relative amount of polysaccharides and aromatic lignin related components in paper mill process waters has been performed using pyrolysis-GC/MS [7, 29].

4.6 Determination and Characterization of Monosaccharide Components in Hemicelluloses

In the first characterization step of hemicelluloses, the kind and quantity of hemicelluloses glycosyl units are usually determined. Mineral, formic or tri-fluoro-acetic acids are commonly used to hydrolyze hemicelluloses. The thin-layer chromatography was mainly used to determine the monosaccharide component. By this method, the identification of monosaccharides is based on visualization of different color with various specific reagents. Laborious preparation and no sufficient resolution in some cases are the main thin-layer chromatography drawbacks [7, 76].

Gas chromatography has showed high potential to determine the sugar components of hemicelluloses. The coupling of gas chromatography with mass spectroscopy facilitates the identification of the biomass degradation products. Several high performance liquid chromatographic techniques have been used for hemicelluloses-carbohydrate analysis. Although these techniques offer higher resolution, the analyzing of saccharides and uronic acids can not be done under the same conditions. Nowadays, capillary zone electrophoresis has been proven to be a valuable tool for carbohydrates analysis. High-resolution separation and reproducible micro-quantification are obtained by on-column detection. However, the detection in nano-scale can be one of the challenging problems, especially in the case of dilute carbohydrates aqueous solution that they have low UV-

absorbance. However, addition of borate to aqueous solution can be used to increase the UV-absorbance [7, 76].

Indirect UV-detection, using sorbic acid as both carrier electrolyte and chromophore is a more sensitive technique to analyse underivatized saccharides in the lower picomole range. In this approach the pH value has to be high enough to achieve proper ionization of the sugars. At pH higher than 12 the concentration of hydroxide ions can not be negligible relative to the concentration of the chromophore. This also influence on the degree of resolution. The high cost of a laser makes the use of indirect fluorescence detection not so efficient [7, 76].

Nowadays, many of new analytical techniques have been developed to determine the composition of monosaccharide. For analysis purposes, the cleavage of the glycosidic bonds between monosaccharide is firstly required. So, different hydrolysis and degradation processes can be applied. Acid degradations can be directly applied on the raw wood while the degradation of delignified wood can be efficiently applied by enzymatic hydrolysis. The degradation of labile uronic acid and other undesirable sugar units is the main problem in acid hydrolysis. Secondly, gas chromatography, high performance liquid chromatography or capillary electrophoresis are applied to analysis the monosaccharides that are produced from hydrolysis processes. Permethylation, hydrolysis or methanolysis, GC-MS are respectively used for linkage analysis. To get valuable information about structure and composition without side effects on sensitive compounds during partial hydrolysis; different NMR spectroscopy techniques give a promising results when they are applied directly on polysaccharides. These techniques are also often employed to determine the fraction and position of O-acetyl groups in acetylated polysaccharides. The linkage sequence can also be determined [9].

5. MEMBRANE FILTRATION OF HEMICELLULOSES

5.1 Basic Principles of Membrane Filtration

The membrane can be defined as a perm-selective barrier between two homogeneous phases. The two phases that are usually considered in the membrane separation are the feed or upstream side phase, and permeating phase or downstream side. Separation depends on the transport ability of one component in feed side through the membrane to permeate side. A schematic representation of membrane separation is presented in figure 5.1 [77, 78].

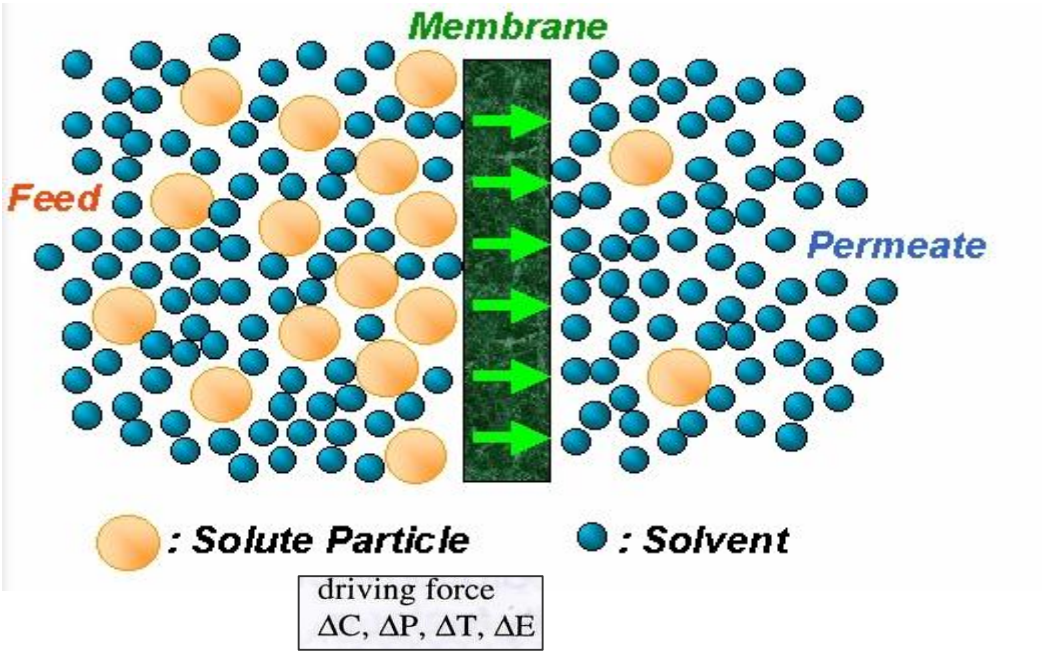


Figure 5.1 : Schematic Representation of Membrane Separation.

The driving forces in membrane separation processes can be a pressure difference or concentration (activity) difference. In some cases, the temperature, chemical potential (μ), and electrical potential difference can also be driving force. Nowadays, various pressure driven membrane processes are used. The concentration or purification tasks can be achieved by the membrane. Aqueous or non aqueous solution with relatively low concentration of solute can be processed by membrane filtration. Chemical properties of solute, size of solute particles and molecules and membrane structure are usually important for the filtration operation. The separation by membrane is achieved by transportation of one component from the feed side to permeate side. The transportation of

this component through the membrane can be because of differences in physical and chemical properties between the membrane and the permeating components [77, 78].

Membranes can be classified in different ways; membranes can be thick or thin. They can have homogenous or heterogeneous structure. The transport by the membrane can be active or passive. The driving force of passive transport can be pressure, concentration or temperature difference [77, 78].

Benefits of the membrane technology

- ü The process is easy and efficient to carry out in continuous mode.
- ü Low energy consumption.
- ü Reliable and easy to combine the membrane processes with other separation processes (hybrid processes such as membrane extraction).
- ü Separation can be carried out under various conditions.
- ü Simple scale up principles.
- ü Separation capability of membranes can be adjust during filtration.
- ü No additives or modifiers are usually required.

Drawbacks

- Ø Fouling and concentration polarisation phenomena that cause flux decline.
- Ø Relatively short lifetime of the polymeric membrane.
- Ø Sometimes insufficient selectivity and flux problems.

The selectivity of the membrane and flow through it are the major parameters that describe the performance and efficiency of the separation by the membrane. Permeate flux or permeation rate is usually used to describe the flow, it is defined as the volume flowing through the membrane per unit area and time. The convective flux through a porous membrane can be defined as:

$$Flux = \frac{driving\ \ force}{vis\cos ity \times total\ \ resistance}$$

In membrane separation, two parameters are usually used to express the selectivity. These parameters are retention (R) and separation factor (α). While the retention is usually used to express the selectivity of the solute in aqueous mixtures; the separation factor is used in the case of gas mixtures [77, 78, 79].

The design of membrane processes consists of pumping section that it used to generate the required driving force and maintain the cross flow velocity. Two types of the membrane process designs can be used. The first one is single stage and the other is multi-stage process. A batch system can be used in the small scale application.

During a pressure driven membrane process, the performance of the membrane separation system often changes with time. The typical behavior of the permeate flux with time decline may be observed. Concentration polarisation and fouling phenomena can usually explain this behavior. The flux decline behavior is more severe in pressure driven membrane process than in gas separation and in pervaporation. Several factors such as adsorption, gel layer formation and pore blocking can decline the permeate flux. These factors induce additional resistances for permeate transports through the membrane. The effect of fouling and concentration polarization phenomena extremely depends on configuration of membrane process and feed solution [77, 78, 79].

5.2 Pressure Driven membrane Processes

The pressure difference is the driving force in the pressure driven membrane processes. The applied pressure must be higher than the osmotic pressure of the solution to achieve transport. The Van`t Hoff equation is usually used to calculate osmotic pressure (π) of the solution is:

$$\pi = c_j \, R \, T \qquad \textbf{(1)}$$

Where c_j: solute concentration (mol/m^3)

R: gas constant = 8.314 J/ (mol K)

T: temperature (K)

The pressure-driven membrane processes that are usually used are microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. In these processes, while the solvent

and some small solute molecules permeate through the membrane by the applied pressure; other molecules or particles are retained by the membrane. The solvent permeation and the solute rejection mainly depend on the structure of the membrane and the size of the solute molecules. The size (or molar mass) of the particles or molecules that can be separated decreases from microfiltration through ultrafiltration and nanofiltration to reverse osmosis. So, the pore sizes in the membrane must become smaller. Smaller pores size increases the mass transfer resistance through the membrane, which means the applied driving force has to be increased to obtain the same flux [77, 78]. The basic principles of the four pressure driven membrane filtration processes are shown in Table 5.1 [80].

When the aim of the separation is the retention of particles with diameter > 100 nm, relatively open membrane structure can be used. The mass transfer resistance in the membrane is low so that the relatively low applied pressure is sufficient to achieve high flux. This membrane process is called microfiltration. If the goal of the process is separation of macromolecules from an aqueous solution, the structure of the membrane is denser that means the hydrodynamic resistance increases, and the applied pressure is higher. This separation pressure is called ultrafiltration [77, 78].

In reverses osmosis the used membranes are very dense (asymmetric), therefore hydrodynamic resistance is very high. The obtained permeate flux is determined by the applied pressure and the membrane resistance (or permeability). In general, the permeate flux through the membrane is inversely proportional to the thickness of the effective layer [77, 78].

Table 5.1: Basic Principles of the Pressure Driven Membrane Filtration [80]

	Reverse Osmosis	**Nanofiltration**	**Ultrafiltration**	**Microfiltration**
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Symmetrical / Asymmetrical
Thickness Thin Film	150 μm 1 μm	150 μm 1 μm	150 -250 μm 1 μm	10 -150 μm
Pore Size	< 0.002 μm	< 0.002 μm	0.2 – 0.02 μm	4 -0.02 μm
Rejection of	glucose, NaCl, amino acids	Mono-,di- and oligosaccharides polyvalent ions,	Macromolecules, proteins, polysaccharides	Particles, suspensions, bacteria
Membrane Material(s)	CA Thin film	CA Thin film	Ceramic , PSO ,PVDF,CA , Thin film	Ceramic PP,PSO ,PVDF
Membrane Module	Tubular, Spiral wound, Plate and frame	Tubular, Spiral wound, Plate and frame	Tubular, Spiral wound, Plate and frame , hollow fiber	Tubular , hollow fiber
Operating Pressure	15-150 bar	5-35 bar	1-10 bar	< 2 bar

5.2.1 Microfiltration (MF)

This membrane process closely resembles conventional filtration. The size range of the particles that can be retained is from 0.05 to 10 μm that means the suspensions and emulsions can be retained. The retention of the solute particles is performed by sieving mechanism. The separation is usually based on solute particles dimensions (shape and size).

Cross flow velocity is used to reduce the effect of additional resistance due to concentration polarization and fouling (deposition of solutes inside the pores of the membrane or at the membrane surface) or gel layer on the membrane surface. The influence of the concentration polarisation and fouling in MF might cause a dramatic permeate flux decline comparing with pure water flux [77, 78, 79].

Large numbers of various polymeric and inorganic materials are usually used to prepare MF membrane. The common used polymers are polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF), cellulosic esters (such as cellulose acetate (CA) and cellulose nitrate), polysulfone (PSO), polyethersulfone (PES), polyamide (PA), polycarbonate (PC) and aliphatic polyamides (e.g. nylon-6). Aluminium oxide (Al_2O_3) titanium oxide (TiO_2), carbon, and various metals are the major inorganic materials that are usually used in preparation of microfiltration membranes [77, 78, 79].

Synthetic polymeric membranes can be divided into two classes hydrophobic and hydrophilic. The fouling tendency is higher in hydrophobic membrane, especially in proteins separation. Furthermore, water can not pass through some very hydrophobic membranes so they can not be wetted by water. In this case, alcohol can be good alternative to pretreat this membranes prior use them with aqueous solutions. The cleaning of membranes must be done periodically to prevent the flux decline. The membrane materials have to be stable for cleaning procedure [77, 78, 79].

Darcy's law is used to describe the permeate flux (J) through the MF membranes. The flux through the membrane is directly proportional to the applied pressure (ΔP).

$$J = A\,\Delta P \qquad \textbf{(2)}$$

The membrane permeability coefficient (A) in this relation contains the effect of the viscosity of the permeating liquid and the effect of structural factors such as porosity and pore size distribution on the permeability through the membrane [77,78].

Removal of suspended solids is the typical application of microfiltration. It can be used as cleaning step in clarification of fruit juice or cold sterilisation of beverages and pharmaceutical and also as concentration step (cell harvesting). Microfiltration is sometimes used as a pre-treatment step for nanofiltration and reverse osmosis for the

production of potable water from ground or surface water, and ultra-pure water in the semiconductor industry. Recovery as colloidal metal oxides or hydroxides, separation of oil-water emulsion, and dehydrations of lattices are also possible applications of microfiltration[77, 78, 79].

5.2.2 Ultrafiltration (UF)

Ultrafiltration process is generally used to retain macromolecules such as proteins, polymers or particles such as colloids and emulsions. The range of molecules sizes that are retained is from 0.05 μm - 100 nm. Salt ions, low molar mass organic solvents and other small solute molecules can freely pass through the UF membrane. The driving pressure that usually applied is between 2 and 10 bars. The separation principle is based on the sieving mechanism, thus UF membranes can be considered as porous membranes. The rejection in UF is mainly determined by the size and shape of the solute molecules. The transport of permeate through the membrane is directly proportional to the applied pressure. Kozeny- Carman equation is usually used to describe the convective permeate flow through a porous UF membranes [77, 78, 79].

Ultrafiltration and microfiltration membranes almost have quite similar separation principle. However, UF membranes usually differ in the structure of theirs layers. They are asymmetric with dense, smaller pore size and lower surface porosity of the skin layer. UF membranes can be made from the same polymeric and inorganic materials that they used in MF. Phase inversion process is usually used for preparation. The hydrodynamic resistance in UF membranes is much higher than in MF. However, the thickness of the top layer of UF membrane is often less than 1 μm [77, 78, 79].

The definition of the permeate flux and the permeability constant in UF processes is the same as in MF processes. However permeability constant of a UF membrane is much lower. In general, the value of permeability constant is around 20 L / (m^2 h bar) for dense membranes and about 200 L / (m^2 h bar) for more open membranes. UF membranes are often used as sub-layer in composite membranes for reverse osmosis and nanofiltration membranes [77, 78, 79].

The selection of suitable UF membrane to concentrate a certain macromolecular solutions is based on cut-off concept (number expressed in g/mol indicating that 90% of the species with a molar mass larger than this value will be rejected). The concentration polarisation and fouling are the major problems in the UF processes. These phenomena occur because of the retained macromolar solutes accumulation on the surface of the membrane and building up the solute concentration. At steady state conditions, the convective solute flow towards the membrane and the back diffusion flow from the membrane surface to the bulk will be equal. The phenomena that take place in the boundary layer determine the process performance [77, 78, 79].

Nowadays, MF and UF membranes with higher chemical and thermal resistance are developed. The membranes become more resistant to higher temperatures (>100ºC) to a wide range of pH (1-14) and to organic solvents. The main applications of UF are as filtration step in dairy and food industry. UF is also used in metallurgy industries, and drinking water production [77, 78, 79].

5.2.3 Nanofiltration (NF)

The most promising application for NF is purification of brackish water and surface water. This process is applied to retain micro-pollutants such as herbicides, and insecticides. Generally, the retention of low molar mass organics in the range of 200 to 1000 g/mol, and multivalent salts such as calcium salts can be achieved by NF. The driving pressure that usually applied in NF processes is in the range 3- 20 bars. The industrial applications of NF are the concentration of product streams with specific components such as proteins, enzymes, antibiotics and dyes. NF is also used to separate low molar mass solutes such as inorganic salts or small organic molecules such as glucose, and sucrose from a solvent. NF membranes can be used for softening the hard water [77, 78, 79].

The volume flux of permeate can be calculated by:

$$J = A (\Delta P - \Delta \pi) \quad \textbf{(3)}$$

Where A: membrane permeability coefficient

ΔP: applied hydrodynamic pressure

$\Delta \pi$: osmotic pressure difference across the membrane

The membrane permeability coefficient (A) depends on the membrane that is chosen. The optimization parameter of the process is the applied pressure (ΔP).

Composite NF membranes are currently used in many separation processes. Interfacial polymerization is applied to form top layer of the membrane. NF membranes are almost similar to reverse osmosis (RO) membranes. While the monovalent salts retention and applied pressure in NF processes is lower than RO, the permeate flux and water permeability are higher. Besides composite membranes asymmetric membrane such as cellulose acetates are used in some cases [77, 78,79].

5.2.4 Reverse Osmosis (RO)

The retention of all low molar mass solutes can be achieved by RO. The RO membranes are used in desalination of seawater. High potable water recovery can be obtained from seawater in single stage operation. Since the osmotic pressure increases in the retentate side, high applied pressure ranging from 20-100 bars is required. The average hydrodynamic pressure in the seawater desalination process is about 60 bars. This pressure can be enough to exceed the osmotic pressure of seawater that is around 25 bars [77, 78, 79].

Retention of low molar mass solvents such as methanol and ethanol is fairly good by RO. However, the rejection of the solutes by RO strongly depends on the type of the membrane. The main industrial applications of the RO are production of ultra-pure water for electronic industry, concentration of fruit juice and sugars in food industry, and concentration of milk in dairy industry [77, 78, 79].

Both asymmetric and composite membranes are used for RO. The structure of the latter membranes is denser than NF membranes. The top layer is formed by interfacial polymerisation reaction. Polysulfone or polyethersulfone, cellulose triacetate and aromatic polyamides are usually used to form support layer of the RO membrane [77, 78, 79].

5.3 Membrane Filtration of Solutions containing Hemicelluloses

Since 1950s the extraction of hemicelluloses from different raw materials has been studied. Various extraction and purification techniques have been proposed to isolate hemicelluloses form their resources. The membrane filtration can be the possible alternative for the separation and purification of hemicelluloses extracted from wood and annual crops.

The thermo mechanical pulping (TMP) of wood is considered one of the promising sources of hemicelluloses. Membrane technology is used to recycle the valuable materials and purify the process water for reuse purposes in pulp and paper industry. Several related studies preformed membrane filtration to isolate hemicelluloses from process water of thermo-mechanical pulping. Persson et al. [81] studied the economic evaluation of the hemicelluloses isolation from the process water of TMP of spruce. They tested the performance of several different membranes to find the most suitable membrane filtration process to separate isolated hemicelluloses. They concluded that the isolation of hemicelluloses from TMP process streams using proper membrane can be beneficial.

Persson et al. [26] investigated the performance of UF membranes to treat process water from thermo-mechanical pulping (TMP) of spruce. They observed that the fouling and flux decline were higher when hydrophobic membranes were used. The highest flux and the most efficient separation between hemicelluloses and contaminants (salts and monosaccharides) was obtained by using hydrophilic membrane C005F (Microdyn Nadir GmbH –cut off 5,000 g/mol).

Ultrafiltration has been shown to be effective in recycling and treatment of wastewater prior to effluent discharge in pulp and paper industry. Lignin recovery from kraft black liquor, concentration of dilute spent sulfite liquor from paper mill, and color removal from kraft mills bleaching effluent are some of the most important applications of the UF. During UF, high molar mass components are retained and concentrated by the membrane while low molar mass components were passed through the membrane. The maximum purification of the desired components can be achieved by diafiltration [82, 83].

Bhattacharya et al. [84] combined biological degradation and membrane separation for the treatment of the pulp mill prehydrolysis effluents. While the biological treatment was used to convert dissolved sugars into suspended yeast, UF was used to remove colloidal particles and suspended yeast. Complete removal of the sugars was achieved using RO filtration process.

Nabarlatz et al. [85] evaluated the performance of ultrafiltration membranes in purification of the xylo-oligosaccharide solutions. They found that the complete removal of lignin-related low molar mass compounds can be achieved by using continuous diafiltration after ultrafiltration. The best results were obtained using polymeric ultrafiltration membranes with cutoff as low as 1,000 g/mol. However, the use of solvent extraction and activated carbon adsorption can be efficient to remove the lignin-related impurities from the xylo-oligosaccharides solutions. Generally, precipitation can be used to extract lignin from kraft black liquor. Ceramic membranes with cut-offs of 5,000 g/mol has been mainly used to purify the lignin fraction from cooking liquor [86, 87].

Wallberg et al. [44] used ceramic ultrafiltration membranes (cut-offs 5,000-15,000 g/mol) and polymeric membranes (cut offs 4,000-100,000 g/mol) to extract hemicelluloses from black liquor. They studied the effect of different parameters such as transmembrane pressure, temperature, and pH on retention. They found that the transmembrane pressure and temperature have a considerable effect of the retention of hemicelluloses during ultrafiltration of kraft black liquor.

Nanofiltration has been extensively studied in the pulp and paper field. Pizzichini et al. [88] tested the performance of different membrane technologies and membrane modules for purification of pulp and paper wastewater. They found the ceramic tubular membrane gives the highest filtration performance, higher productivities and lower fouling. Nevertheless, treatment of effluents from the alkaline extraction stage of pulp bleaching using both polymeric and ceramic membranes is one of important membrane applications in pulp and paper industry. Several studies showed that the utilization of NF without pretreatment by UF is more cost efficient in purification this type of effluent. Treatment of paper mill effluent in single stage nanofiltration was developed by Mänttäri et al [89]. They tested different membranes at laboratory scale and the performance of the used

membranes was evaluated by measuring the permeate flux and contaminant reduction. In their study, the Desal-5 (Desalination Systems- GE-Osmonics) and NF 45 (FilmTec-Dow) membranes satisfied stable and high permeate flux, acceptable reduction and low fouling effect.

Jokinen and Nyström [90] tested and compared the efficiency of the micro-, ultra- and nanofiltration on laboratory and pilot scale to treat process water of paper mill. They used the reduction of certain measurable parameters by the membrane to evaluate the performance of different membranes and modules. They found the UF process can be more reliable as a pretreatment for NF in the term of reduction of certain measurable parameters in the feed solution. Higher flux was obtained by using cross rotational (CR) module in UF. However, NF without pretreatment step generally gave better reduction values.

Persson et al. [91] developed separation method to extract hemicelluloses from process water of masonite production. Their method was carried out in three steps. The first step was the removal of high molar mass molecules and suspended species by MF. The second step was preconcentration of hemicelluloses by UF and the last one was purification and reduction of the of salts and monosaccharides concentration by diafiltration. In that method, partial retention of hemicelluloses was observed during MF. The selection of suitable membrane for the ultra and diafiltration of process water of thermo-mechanical pulping of spruce had great importance. The average flux they obtained by MF was 75 L/m^2 h and by UF was 38 L/m^2 h. In their experiments, the fouling behavior was observed during both MF and UF. They concluded that the reasons of low hemicelluloses recovery by MF were fouling effect, and adsorption and interaction with cellulosic and hydrophobic membrane materials. High retention of hemicelluloses during preconcentration step indicated the treatment of high hemicelluloses concentration solution can be possible by using UF. The previous study [92] showed that the fouling during separation of hemicelluloses from process water of thermo-mechanical pulped spruce was significant with polyethersulphone (PES) hydrophobic membranes. Higher separation efficiency between hemicelluloses and monosaccharides and salts was obtained by membrane with cut-off 5,000g/mol than membranes with 1,000 g/mol.

Schlesinger et al. [93] investigated the performance of five alkali resistant polymeric nanofiltration and tight ultrafiltration membranes to separate hemicellulose from process liquors of viscose fiber production. They emphasized to use the operating conditions of real processes to clarify the relative differences of the membranes and optimization operating pressure and temperature. Their experiments showed that the polyethersulfone-type membranes can be used to retain hemicelluloses with molar masses above 1,000 g/mol. However, nanofiltration membranes can be successfully applied for efficient separation of hemicellulose and sodium hydroxide. The N30F (Microdyn-Nadir) and G-5 (GE-Osmonics) membranes had the ability to separate hemicellulose and sodium hydroxide efficiently.

Gabrielii et al. [14] separated hemicelluloses from aspen wood by using combination of alkali extraction processes with ultrafiltration. Molar mass, sugar composition, and amount of acidic groups were determined to characterize the hemicellulose product. Relatively high molar mass hemicelluloses with narrow molar mass distribution were obtained. The process scheme used for hemicelluloses recovery is shown in Figure 5.2. The hemicellulose product did not contain acetyl groups and only small amounts of lignin remained in the recovered hemicelluloses. The hemicelluloses product was significantly soluble in hot water.

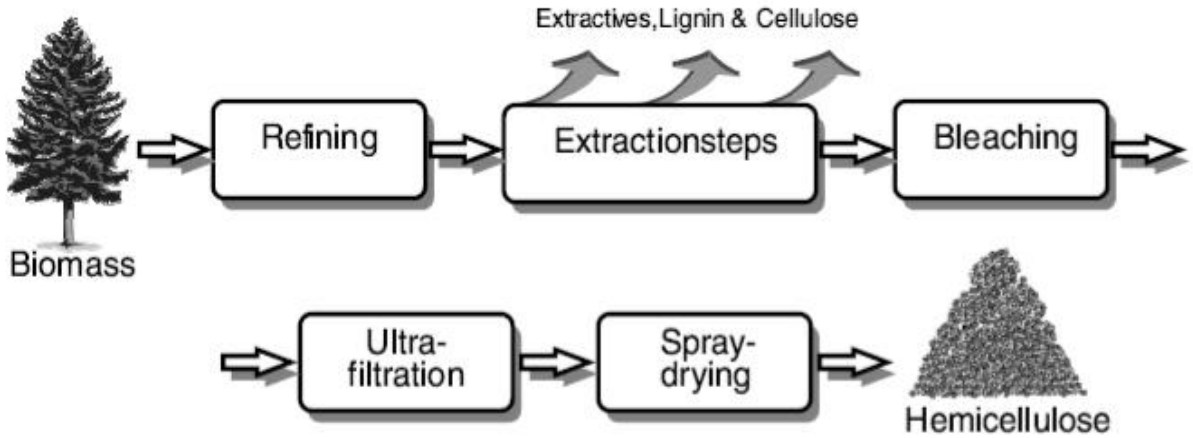


Figure 5.2: The Process Used for Hemicellulose Recovery [13]

Nanofiltration membranes with cutoffs from 150 to 1,000 g /mol can offer promising separation techniques for hemicellulose hydrolyzes. The cost efficiency and ease to use give NF advantages compared to chromatographic methods. NF membranes with cut-offs

of 150–300 g /mol were useful to concentrate xylose. Recovery of d-xylose into the permeate from a hemicellulose hydrolyzate stream by nanofiltration was evaluated by Sjöman et al. [94, 95]. In their study the effect of operating pressure and temperature, and the effect of feed composition on the recovery of xylose were investigated. Their results showed that the NF separation can efficiently purify xylose from hemicellulose hydrolyzate.

Several studies have been aimed to test the effect of hemicellulose composition and sub-molecular structure on nanofiltration performance parameters such as permeate flux, hemicellulose retention and fouling effect. The fouling behavior during NF of real effluents from the pulp and paper industry showed that the retention of anionic substances was better with less fouling effect because of charge repulsion effect at high pH where the charge of most NF membranes is negative [96].

During nano- and ultrafiltration of alkaline solutions containing hemicelluloses, hemicellulosic gel layer on the surface of ultrafiltration membranes can be generated by applied pressure compressing. The formation of gel layer can be controlled by cross flow velocity. The aggregation behavior of hemicellulose in strongly alkaline solution plays an important role in the gel layer formation during nano and ultrafiltration. However, the formation of this layer increases the hemicellulose retention [96].

Andersson et al. [27] compared the utilization of diafiltration and size-exclusion chromatography (SEC) as purification techniques of hemicelluloses. The schematic illustration of the method they used to isolate hemicelluloses from the process water is shown in figure 5.3. The SEC method can be used to evaluate the retention of substances below 1,000 g/mol. The goal of their study was isolation of hemicelluloses from smaller molar masses compounds such as small oligosaccharides, monosaccharide, and salts. They used purity, recovery, and size distribution of hemicelluloses as the comparison parameters between diafiltration and SEC. However; the results indicated that high oligo- and polysaccharides recovery can be achieved using both purification methods. Increasing the purity by diafiltration can be performed by adding more dia-volumes. Diafiltration can probably be the most cost-efficient purification method for the extracted hemicelluloses from this process water.

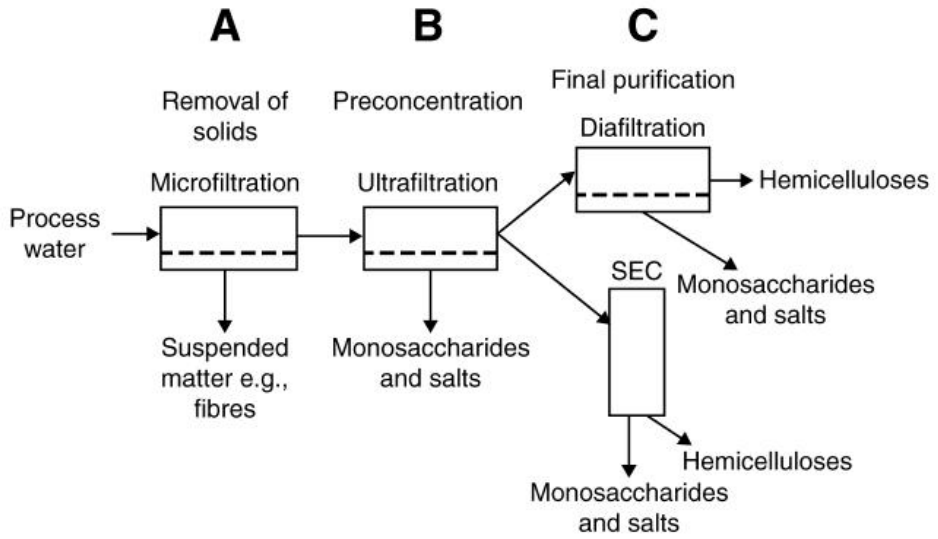
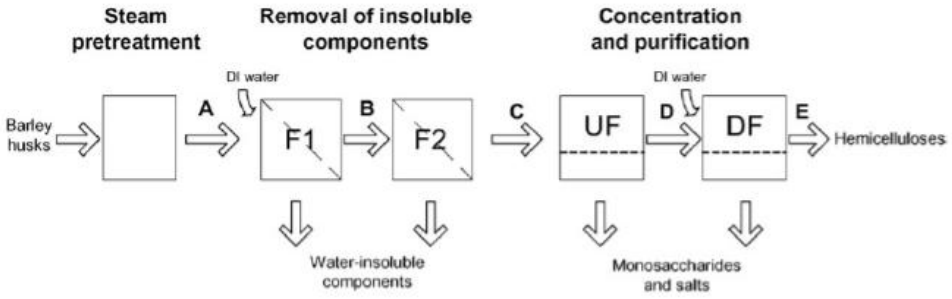


Figure 5.3: Schematic Illustration of the Isolation Method of Hemicelluloses from the Process Water from Thermo-mechanical Pulping of Spruce [27]

The integration between bioreactor process and membrane separation was developed where the beech-wood xylan was investigated as feed stock in oligosaccharide production from agricultural residues. This membrane reactor operation offers effective hydrolysis simultaneously with fractionation in two streams with different molar mass ranges of oligosaccharides. Membrane reactor system can be a promising method for enzymatic hydrolysis. In this system hydrolyzed products permeate through the membrane, whereas cellulolytic enzymes and unhydrolyzed cellulosic materials are retained [97, 98]. Krawczyk et al. [19] isolated arabinoxylan from barley husks. In their work hemicelluloses were extracted by steam explosion. The separation of extracted hemicelluloses was performed by ultrafiltration, and the diafiltration was used for further purification. They used composite fluoro-polymer membrane (cut-off of 10,000 g/mol) during UF and diafiltration. The volume reduction (VR) value was 0.85 (VR is known as the ratio between the volumes of permeates and the initial feed volume). The average flux during UF and diafiltration was 90 L/m^2 h and 50 L/m^2 h, respectively. Polysaccharides content was about 40% of the solids fraction before ultrafiltration and approximately 70% after diafiltration. The fraction of arabinoxylan after diafiltration was 45% of the polysaccharide fraction. The schematic illustration of the isolation process is shown in figure 5.4.



Solution	Specifications
A	Total solid (TS) content = 21.0 wt% Concentration of oligo and polysaccharides = 21.5 g/L MM_{av} = 24,000 g/mol
B	TS content = 1.9 wt% Concentration of polysaccharides = 5.5 g/L
C	TS content = 1.2 wt% Concentration of polysaccharides = 4.8 g/L (40.0 % of the solid fraction)
D	Concentration of polysaccharides = 31.5 g/L
E	Polysaccharides fraction = 70.0 % of the solid fraction MM_{av}= 54,000g/mol

Figure 5.4: Schematic Illustration of the Hemicelluloses Isolation Process fromBarley Husks. (DI: Deionised Water. F1, F2: Filtration Units) [19]

Heat treatment of solutions containing hemicelluloses can cause hemicelluloses degradation that means average molar mass decreases so that the flux enhances but the retention reduces. Addition of hydrogen peroxide revealed similar effects. Low average molar mass hemicelluloses fraction reduces the fouling effect so the ability to form hemicellulosic gel layer on the membrane surface decreases [96].

The content of hardwood compounds that contain acetyl groups is approximately 3.5 % by mass. Those compounds can be hydrolysed to acetic acid. Membrane technology can efficiently separate the generated acetic acid from the wood chips during hot water pretreatment. By this pretreatment, the delignification of the wood chips is easier [46, 99].

EXPERIMENTAL WORK

This study focus on developing the suitable set of membrane filtration processes to produce hemicellulose fractions with high enough concentrations that they can be used in various applications such as bio-ethanol production. The performance of various flat sheet, thermally stable membranes in the concentration and purification of the extracted hemicelluloses by hot water extraction was investigated. The suitable operating conditions, specifications and efficiency of the used membrane separations processes were also determined.

6. EQUATION AND MATHEMATICS

Ø The mass flux (J_m) can be determined by :

$$J_m = \frac{m_p}{A_m} \quad \textbf{(4)}$$

Where

m_p: mass flow rate of permeate (Kg/h)

A_m: membrane surface area (m^2)

Ø The selectivity of the membrane for a solute is described by rejection.

The rejection which can be observed (R_o) is defined by equation:

$$R_o = 1 - \frac{c_p}{c_b} \quad \textbf{(5)}$$

Where

c_p: concentration of solute in permeates.

c_b: concentration of solute in the solution on high pressure side of membrane (feed side).

Analytically:

- The salt rejection is calculated based on the conductivity in permeate and feed
- The organic matters, hemicelluloses ,lignin and monosaccharide rejection can be calculated based on the total organic carbon (TOC) content, total carbohydrates content, UV absorbent and turbidity of permeate and feed samples.

Ø In this study the fouling was determined based on the difference between the pure water flux before (PWFb) and after (PWFa) the process solution filtration.

$$\text{Fouling (\%)} = \frac{PWFb - PWFa}{PWFb} \cdot 100\% \quad \textbf{(6)}$$

Ø The removal of organics, lignin, hemicelluloses and monomeric sugars by diafiltration was calculated as :

$$\text{Removal (\%)} = \frac{m_b - m_a}{m_b} \cdot 100\% \quad \textbf{(7)}$$

Where

$m_{b:}$ content of the compound in concentrate before diafiltration (g)

m_a: content of the compound in concentrate after diafiltration (g)

Ø The separation of monomeric sugars from hemicelluloses can be defined using separation factor concept. Monomeric sugars separation factor (X_{mono}) is a measure of monomeric sugars purification from hemicelluloses. This factor indicates the change in the ratio of the monomeric sugars to hemicelluloses in permeate compared to the ratio between them in feed. The value of this factor has to be greater than 1 to indicate the separation of monomeric sugars from hemicelluloses

$$X_{mono} = \frac{1 - R_{mono}}{1 - R_{hemi}} \quad \textbf{(8)}$$

Where

R_{mono}: retention of monomeric sugars

$R_{hemi:}$ retention of hemicelluloses

7. MATERIALS AND METHODS

7.1 Raw Materials

The solutions used in the study were pressurized hot water extraction liquors from spruce saw dusts. It can be described as brown liquid. The extraction solutions and the solid samples were prepared by Finnish Forest Research Institute (Metla). The extraction liquor batches contained oligo- and polysaccharides (mainly hemicelluloses) and monosaccharides with different concentrations. The dominating hemicellulose in spruce is O-acetyl galactoglucomannan (GGM). Table 7.1 shows the main specification of the used solutions.

Table 7.1: Specification of the Extraction Liquors (E.liquors)

Feed	EXP #	Concentration (g/L)	Hemicelluloses (%)	Monomeric Sugars (%)	Average Molar Mass (g/mol)
E. Liquor at 175 - 180 ºC	1	5.1 g/L Hemicelluloses 0.8 g/L Monomeric sugars	–	–	–
E. Liquor at 170ºC	2	10	71	9	2,600
E. Liquor at 170ºC	3,4,5, 6	10	82	9	3,000

7.2 Membranes

Microfiltration of the feed solution was performed using MV020 membrane to remove solids and fibers.UC005, UC010 and UC030 are hydrophilic ultrafiltration membranes with various cut-offs, and they were used to concentrate and fractionate high molar mass components (mainly hemicelluloses) in the extraction solutions. They were also used for purification of the retained hemicelluloses by diafiltration. Those hydrophilic membranes are usually usable for aqueous solution filtration.

The tight ultrafiltration membranes (TUF) were used for concentration of low molar mass hemicelluloses. In this study GE-10, GE-5, and ETNA01PP were selected. While GE-5, GE-10 membranes are relatively hydrophilic; the hydrophilicity of ETNA01PP membrane is higher. Table 7.2 represents the main properties of the used membranes.

Table 7.2 : Main Specification of the Used Membrane

Membrane	**Process**	**Manufacturer**	**Membrane Material**	**Nominal Pore Size (µm) / Cut-Off (g/mol)**
MV020	MF	Microdyn-Nadir GmbH	Poly-vinylidene-fluoride (PVDF)	0.2
UC005	UF	Microdyn-Nadir GmbH	Regenerated Cellulose (RC)	5,000
UC010	UF	Microdyn-Nadir GmbH	Regenerated Cellulose (RC)	10,000
UC030	UF	Microdyn-Nadir GmbH	Regenerated Cellulose (RC)	30,000
GE-10	TUF	GE- Osmonics	Proprietary	2,500
GE-5	TUF	GE- Osmonics	Proprietary	1,000
ETNA01PP	TUF	Alfa Laval	Composite Fluoro Polymer (PVDF) on Polypropylene	1,000

7.3 Filtration Equipments

The Millipore stirred cell (volume = 300 ml) was used to carry out pre-experiments. The active surface area of the membrane sheet was 40 cm^2. The dead end filtration occurred in this unit.

The major filtration experiments were carried out using a flat sheet lab scale membrane filtration unit with an active surface area of 100 cm^2. The flow mode in this filtration unit was cross flow. Figure 7.1 represents the illustration scheme of the membrane filtration process.

In this cross flow filtration system the feed solution was pumped from the feed tank (volume 3.0 L) to the membrane module by using Hydra-cell pump (Manufacturer: WANNER Engineering INC) that applied the trans-membrane pressure in the system. Vacon frequency converter was used to control the flow by the pump. The pressure over the membrane can be varied from 0 to 25 bars by using control valve. During filtrations the retentate flowed back to the feed tank and the circulation flow rate was measured with flowmeter. The permeate flux was measured gravimetrically with a balance. The calculation of the permeate flux through the membranes were based on equation # 4, where the osmotic pressure difference between feed and permeate was neglected. The circulation flow was maintained in turbulent regime to avoid concentration polarization effect. The cross flow velocity and the applied pressure in the system were adjusted depending on the cut-off of the membrane. All filtration experiments were carried out at 70ºC.

In addition to the original extraction liquor, some of the feed solution was prepared in the laboratory by dissolving 10 g of the dry solid samples of extracted compounds (mainly hemicelluloses) in one liter of water.

The filtration runs were performed with the selected membrane to investigate the membrane ability to concentrate and purify hemicelluloses as a function of the membrane cut-off and chemical nature when the feed concentration and temperature are constant. The pure water flux (PWF) tests were carried out at the beginning and at the end of the run (after filtration and flushing) to detect the effect of concentration polarization and intensity

of the membrane fouling. The reduction in the pure water flux, which is a measure of membrane fouling, was calculated by comparing the pure water flux before and after the filtration (based on equation # 6).

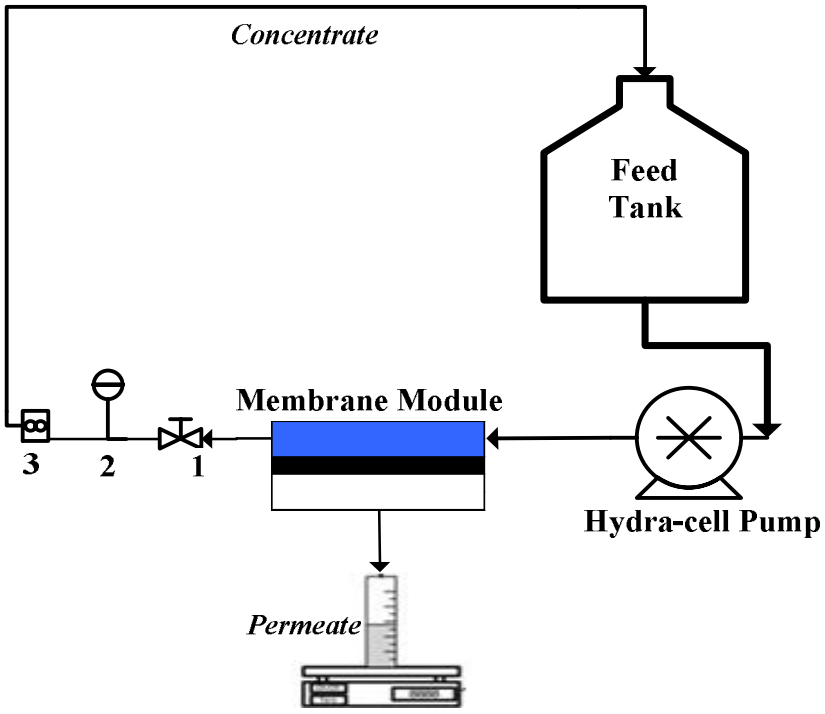


Figure 7.1: Illustration Scheme of the Used Membrane Filtration Process
1: control valve, 2: pressure gauge, 3: flow meter.

7.4 Membrane Filtration Experiments

7.4.1 Microfiltration

For some solutions the solids (mainly fibers) were removed by microfiltration. The filtration module was equipped with MV020 membrane (Microdyn Nadir GmbH) with a mean pore size of 0.2 µm. The membrane filtration was performed at a trans-membrane pressure between 1 -2 bars at 70 ºC and rotor speed in stirred cell was about 250 rpm.

7.4.2 Ultrafiltration and Diafiltration

Before using the UF membrane, the recommended pre-treatment method of membrane from the manufacturers using water or ethanol was performed. Different sets of membrane processes were performed to maximize hemicelluloses retention through the experimental scheme. The filtration procedure to isolate hemicelluloses from the extraction liquors involved three steps: removal of solids and fibers by microfiltration (if needed), concentration of high molar mass hemicelluloses by ultrafiltration and low molar mass hemicelluloses by tight ultrafiltration then purification of the retained hemicelluloses by diafiltration. In this process the concentration of the filtrate was increased by taking permeate out while the retentate was recycled back to the feed tank until the sufficient volumetric concentration ratio (VCR) was reached (VCR is defined as the ratio between the volume of initial feed and the concentrate volume). Batch diafiltration was used for further purification of the isolated hemicelluloses. During diafiltration, certain volume of RO filtered water (κ = 0.054 μS/cm, T = 25 ºC) was added several times to the concentrate in the feed tank and it was removed at about the same volume as permeate. Different ratios between the volumes of the added water to the concentrate volume were used. The water was added until relatively clear permeate was obtained. Feed, concentrate and permeates were sampled form each filtration experiment. In this work, the experimental scheme in the main experiments was performed as follows (Figure 7.2):

First Step: Concentration and purification of high molar mass compounds (mainly hemicelluloses) from the original feed solution using membranes with higher cut-off (5,000, 10,000 or 30,000 g/mol- UF membranes).

- Measuring of the pure water flux through the membrane at 70ºC.
- Filtration of the original feed solution and measuring permeate fluxes at 70ºC.
- Purification of the concentrate by adding pure water (diafiltration) and measuring permeate fluxes at 70 ºC. (Volume of added water to the concentrate volume for each diafiltration stage was 1:1 and in some cases 2:1).
- Measuring of the pure water flux through the membrane after filtration at 70ºC.
- Taking samples for feed, concentrates and accumulated permeates.

Second Step: Separation of monomeric sugars from low molar masses hemicelluloses from permeates of higher cut-off membrane using membranes with lower cut-off (1,000 or 2,500 g/mol-TUF membranes).

- Measuring of the pure water flux through the membrane at 70ºC.
- Filtration of the UF membrane permeates and measuring permeates fluxes at 70ºC.
- Purification of the concentrate by adding pure water (diafiltration) and measuring permeate fluxes at 70 ºC. (Volume of added water to the concentrate volume for each diafiltration stage was 1:1 and in some cases 2:1).
- Measuring of the pure water flux through the membrane after filtration at 70ºC.
- Taking samples for feed, concentrates and permeates.

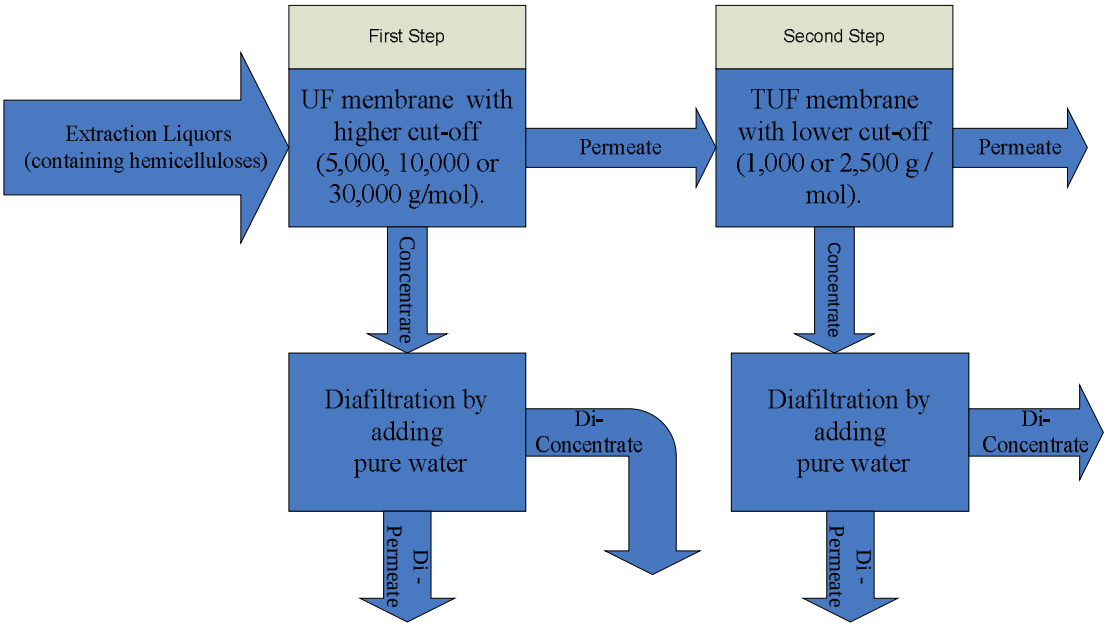


Figure 7.2: Illustration Schemes of the Filtration Experiments

Six major experiments were performed using the flat sheet module. The operating pressure, and the cross flow velocity were adjusted and the purification efficiency by diafiltration was investigated in the first two experiments. The ability to maximize the hemicelluloses retention and purification by diafiltration using different sets of ultrafiltration and tight ultrafiltration membranes was examined in the experiments # 3,4,5,6 where the same extraction liquor was used as the original feed solution. Table 7.3 shows the main specification and operating conditions for the major experiment sets.

Table 7.3: Operating Conditions of the Main Filtration Experiments

EXP #	Step	Used Membrane	Pressure (bar)	Cross flow Velocity (m/s)	Original Feed Solution
1	**a**	**UC005**	3→5	2.1→2.8	E. Liquor (5.1g/L) hemicelluloses.
	b	**GE-5**	10→20	2.8→3.1	
2	**a**	**UC005**	3.5	1.8	E. Liquor (7.1%) hemicelluloses.
	b	**GE-5**	10	2.8	
3	**a**	**UC030**	1	1.6	E. Liquor (8.2 %) hemicelluloses
	b	**GE-5**	10	2.8	
4	**a**	**UC010**	3	1.9	E. Liquor (8.2%) hemicelluloses
	b	**GE-10**	7	2.8	
5	**a**	**UC005**	3.5	2.1	E. Liquor (8.2 %) hemicelluloses
	b1	**GE-5**	10	2.8	
	b2	**ETNA01PP**	12.5	2.8	
6	**a**	**UC030**	1	1.6	E. Liquor (8.2 %) hemicelluloses
	b	**ETNA01PP**	10	2.8	

7.5 Analysis Methods

Samples from feed, permeates and concentrates streams were taken for analysis. Centrifugation of feed and concentrates samples were done to precipitate and remove suspended solids and fibers before analysis. To calculate hemicelluloses, lignins and organics retention and evaluate the purification efficiency, all liquid streams were analyzed regarding to organics, total carbohydrates, and monosaccharide content, and ultraviolet (UV)-absorbance.

The total organic carbon (TOC) measurements that were used to determine organic solute concentration was done using TOC-5050 analyzer. Lignin residuals (contain phenolic groups which absorb UV light) contents were detected at the absorption light with wavelength of 280 nm using Cary UV-Visible spectrophotometer. The total carbohydrate contents were measured using anthrone-sulfuric acid color method. The samples for these measurements were diluted with RO filtered water**.**

Detailed analysis was done in Metla research center to measure the hemicelluloses and monomeric sugars concentration. This analysis was carried out on freeze dried samples using methanolysis – GC method [74]. The lignin content was measured by correlated the

lignin concentration with UV absorbent at 280 nm. The dried samples were firstly pretreated by methyl-tertbetylether extraction to remove extractives.

The pH and conductivity were measured to determine the ionic content of the samples. The conductivity was measured with a digital conductivity meter (Konduckto meter 703) calibrated with 0.01M KCl. The presence of suspended solids and possibly extractives and lipophilic compounds was detected by measuring turbidity using 2100ANIS turbidi-meter.

8. RESULTS AND DISCUSSION

8.1 Permeate Flux and Fouling Ability during Concentration of Hemicelluloses

The permeate flux is one of the most important parameters to evaluate the performance of membrane filtration processes. When the required level of solute retention is obtained, the permeate flux becomes a fundamental factor in the optimization of the process. It is also important to make it compatible with the industrial reality. The higher permeate flux means the lower membrane area is needed to process a certain amount of solution.

The preliminary experiments were carried out in dead end filtration mode to study the behavior of the extraction liquor during filtration by various sets of ultrafiltration membranes with different cutoff. The effect of the temperature and the pretreatment of the liquor by microfiltration on the permeate flux was investigated. The flux measurement results showed that the permeate flux increases when the temperature increases. The pretreatment of the feed solution by microfiltration was useful to retentate solids particles and suspended matters and to improve the permeate flux in the further ultrafiltration stages. The highest average permeate flux through the UC030 membrane was 84 kg/m^{2}h at 2 bars, and the highest average permeate flux through the UC010 and the UC005 membrane was 85 kg/m^{2}h at 3 bars and 78 kg/m^{2}h at 4 bars, respectively, when the extraction solution was pretreated by MF. On the other hand, the highest average permeate flux through the UC030 membrane was 33 kg/m^{2}h at 2 bars, and the highest average permeate flux through the UC010 and the UC005 membrane was 82 kg/m^{2}h at 3 bars and 70 kg/m^{2}h at 4 bars, respectively, when the extraction solution was not pretreated. The

accumulation of the suspended solids and particles on the surface of the UC030 membranes can be one of the possible reason for the low permeates flux that was obtained when they were directly used.

Pure water permeability values before and after filtration were used to detect the fouling effect. A substantial difference in the pure water permeability (PWP) was observed in the UC005 membranes. The reduction in pure water flux through the UC030 membrane was moderate while it could be negligible in the UC010 membrane. However, because the membrane surface materials are the same (regenerated celluloses- relatively hydrophilic); the differences in the thickness and cut-off of the membranes can explain the difference in fouling effect in those membranes. High fouling effect in the UC005 membrane may mean the molar mass of the extraction liquor compounds (mainly hemicelluloses) was slightly higher than the cut off of this membrane so they retained by the membrane (high retention) and accumulate on the membrane surface even may block the membrane surface pores. **The detailed results of the feed solution fluxes and pure water permeability (PWP) for pre-experiment are shown in the appendices (I and II).**

The main filtration experiments were performed using the cross flow module. The permeate fluxes were monitored throughout the filtration experiments in order to investigate the filtration behavior of the extraction liquor. The certain mass of the permeate were collected and the fluxes were calculated by dividing the mass of the collected permeate by the collection period and the effective membrane area (equation # 4). The slight change in the permeate flux was observed during concentration higher molar mass hemicelluloses (increasing VCR value) using the UF membranes. Same trend could be observed when the TUF membranes were used to filter the UF permeate and concentrate of lower molar mass hemicelluloses.

The reduction in the permeate flux with time was studied. At the same VCR value, the average permeate flux (J_{av}) was considered to study the behavior of the permeate flux. Figures 8.1 and 8.2 show the behavior of permeates flux during the two stages of filtration (UF then TUF) in the experiments 3, 4, 5 and 6.

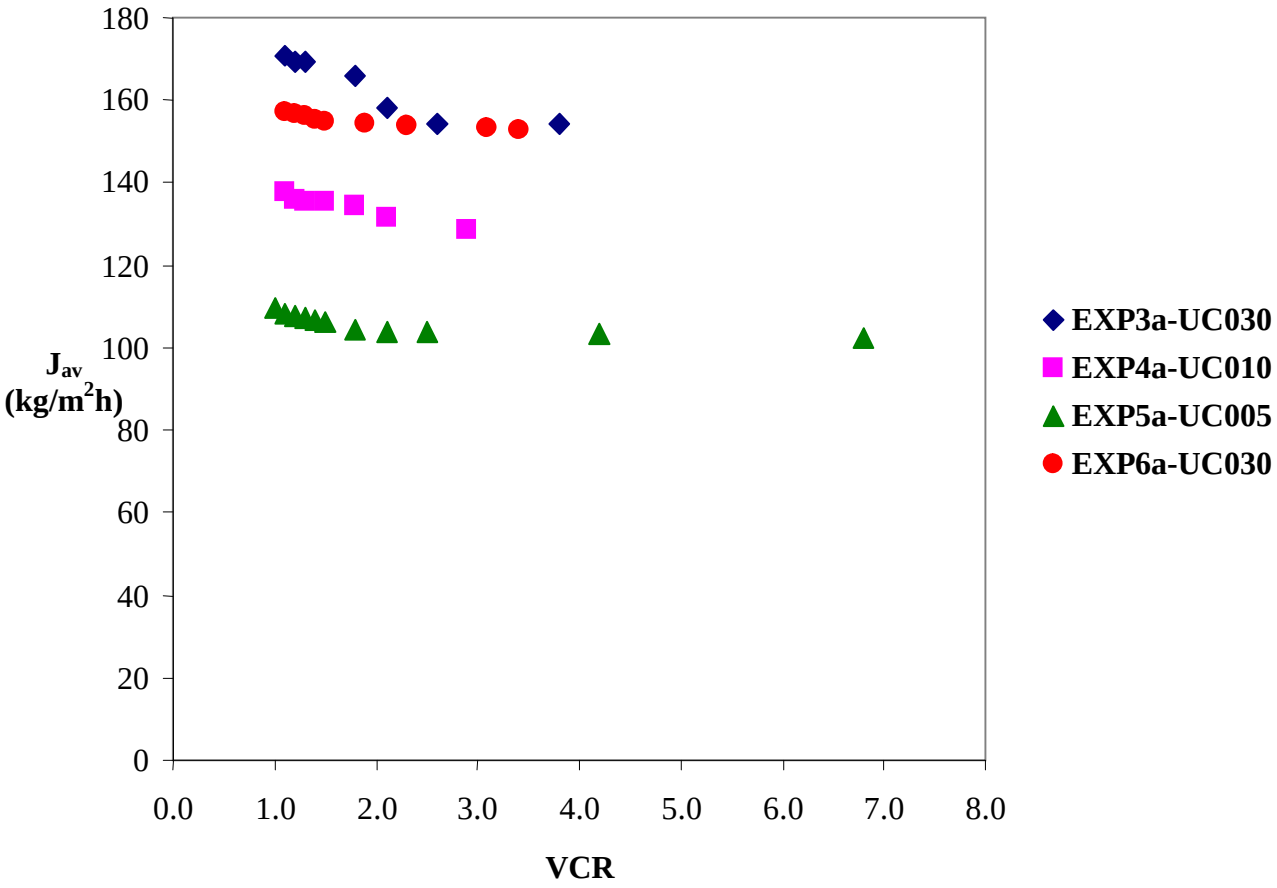


Figure 8.1: Behavior of the Permeate Flux during Concentration of the Feed Solution Using Different UF membranes. T = 70 °C (operating pressure and cross flow velocity are shown in table 7.3)

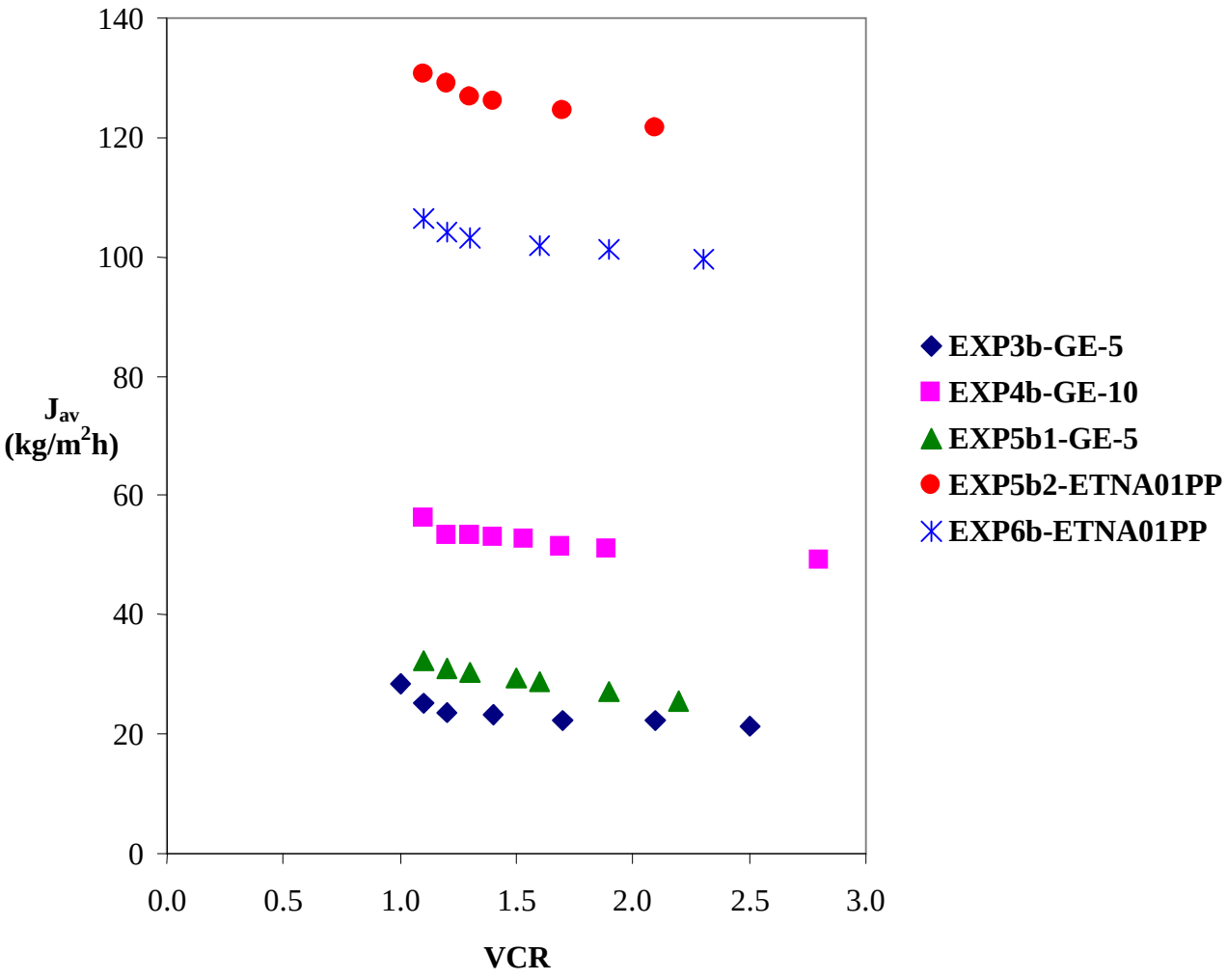


Figure 8.2: Behavior of the Permeate Flux during Concentration of the UF Permeates Using Different TUF membranes. T = 70 ºC (operating pressure and cross flow velocity are shown in table 7.3).

The average permeates flux and the fouling percentage in UF and TUF membranes that were respectively used for the first and second filtration stage are shown in the table 8.1.

Table 8.1: Average Permeate Flux and Fouling Percentage of the Membrane Used in the First and Second Filtration Stages

EXP #	UF-First Filtration Stage			TUF-Second Filtration Stage		
	Used Membrane	**J_{av}(kg/m^{2}h) at (P(bars))**	**Fouling (%)**	**Used Membrane**	**J_{av}(kg/m^{2}h) at (P(bars))**	**Fouling (%)**
1	**UC005**	86 at 3 bars	11	**GE-5**	26 at 10 bars	41
2	**UC005**	83 at 3.5 bars	17	**GE-5**	33 at 10 bars	42
3	**UC030**	165 at 1 bar	18	**GE-5**	24 at 10 bars	30
4	**UC010**	135 at 3 bars	14	**GE-10**	53 at 7 bars	11
5	**UC005**	107 at 3.5 bars	18	**GE-5**	30 at 10 bars	32
				ETNA01PP	127 at 12.5 bars	19
6	**UC030**	155 at 1 bar	22	**ETNA01PP**	103 at 12.5 bars	23

In the first filtration stage, the surface material of the used ultrafiltration membranes was the same. The cut off was only the main difference between them. The results showed that the UC030 membrane (highest cut-off) has the highest permeate flux at lower applied pressure. The high flux through the UC030 membrane can probably lead to higher fouling ability than other used UF membranes where the effect of the pores blocking of the UC030 membrane with large solid particles might be higher.

In the second filtration stage, the differences between the used tight ultrafiltration membranes were the cut-off and the membrane surface materials. GE-10 and GE-5 membranes have the same surface material. The cut off of the GE-10 membrane is higher so its permeate flux was higher than GE-5 even at lower applied pressure. The fouling ability of GE-10 membrane was the lowest even in the cases that the feed solutions of the other TUF membranes were permeates of the UC005 membrane (lowest cut off). High

fouling effect in the GE-5 membrane may mean the accumulation of its feed compounds mainly hemicelluloses) on the surface was higher regardless on the origin of its feed solution. This observation indicates that the feed solution mainly contains compounds with molar mass higher than 1000 g/mol.

GE-5 and ETNA01PP membranes have almost the same cut-off. According to manufacturer, the differences between them can be in the hydrophilicity of the membrane material. The choice of the ETNA10PP membrane was based on the results from previous investigations of isolation of hemicelluloses [26, 27]. The use of this membrane aimed to avoid fouling problems. The filtration experiments showed that the permeate flux through ETNA01PP membrane was obviously higher than other TUF membranes. The fouling ability of this membrane was lower than GE-5 membrane in spite of the applied pressure was higher. It presents relatively larger resistance to fouling, probably due to the medium size of its pores, smaller adsorption of the feed solution, and also as a consequence of a smaller physical-chemical affinity between feed liquor and the material used to prepare the membrane. In general, the flux through the GE-5 and ETNA01PP membranes was higher when theirs feed solution was permeates of the UC005 membrane. However, although the retention of the hemicelluloses was relatively high, the fouling ability in the used membrane was moderated. This means the extraction liquor did not have high fouling effect and the accumulation of hemicelluloses on the membrane surface had a minor effect on the permeate flux.

8.2 Purification of Retained Hemicelluloses by Diafiltration

The main goal of diafiltration was to purify of the retained hemicelluloses by dilution of the UF or TUF concentrate with water and then collecting the corresponding amount of permeates.

During diafiltration the permeate flux dropped to the lower values when the purification proceeds. Removal of lignins, carbohydrates, and other organic compounds by diafiltration of UF concentrate was achieved in different proportion. High removal percentage difference means better separation capability between various compounds. The removal of different compounds increases when higher volume of diafiltration water was added. The removal of lignin-related compounds by the UC010 membranes (EXP# 4)

was higher where the amount of the added water was larger than other cases. The removal of lignin-related compounds by UC030 membrane was higher than by the UC005 membrane where the feed solution and the volume of the added diafiltration water were the same.

The removal of carbohydrates (mainly hemicelluloses) and other organics by diafiltration was typically in the following order (UC030 > UC010 >UC005) regardless on the volume of the pure water added during filtration. The removal of compounds that cause turbidity (such as extractives and lipophilic compounds) was usually low by diafiltration using UF membranes. In some cases, the turbidity in the feed did not change by diafiltration.

In the second filtration stage using TUF membrane the highest removal of lignin-related compounds and other organics was achieved using the ETNA01PP membrane (EXPs# 5, 6). The diafiltration using the ETNA01PP membrane showed that the removal of lignin-related compounds, extractives and other compounds that cause turbidity was higher when its feed solution was the permeate of the UC030 membrane (EXP# 6) while the removal of hemicellulose and other organics was higher when its feed solution was the permeate of the UC005 membrane (EXP# 5).

The removal of hemicelluloses by the GE-5 membrane was the lowest regardless the volume of the diafiltration water and the source of its feed solution (EXPs# 3, 5). The removal of different compounds using the GE-5 membrane when its feed solution was the permeate of the UC005 membrane (EXP #5) was higher than when its feed solution was the permeate of the UC030 membrane (EXP# 3). The possible reason was higher volume of diafiltration water was added (EXP # 5- two times more).

The removal of extractives and other organics that cause turbidity was usually high. The lowest removal of those compounds was obtained when the value of the concentrate turbidity was low (EXP #5 – ETNA01PP). However, the removal of lignin, carbohydrates and other organics was obtained by the GE-10 membrane (EXP# 4) was slightly higher than with the GE-5 membrane (EXPs# 3,5) in spite of on the volume of the added water during diafiltration by the GE-5 membrane was higher in the EXP# 5.

The best purification for the retained hemicelluloses from lignin by diafiltration during the first filtration step was achieved using the UC010 membrane (higher diafiltration water). The diafiltration during the second filtration step was more efficient to remove lignin from the retained hemicelluloses. The GE-5 (EXP# 5) and ETNA01PP (EXP# 6) membranes gave the highest purification efficiency of hemicelluloses (The ratio between lignin removal and hemicellulose removal = 6).

The results showed that the chemical nature of the TUF membranes and the membranes cut offs have the significant effect on the efficiency of the diafiltration to purify hemicelluloses from other compounds especially lignin. Tables 8.2 and 8.3 show the permeate fluxes during diafiltration and removal percentage of various compounds through diafiltration in the both filtration stages. **The detailed results of analysis measurements are shown in the appendix (V).**

Table 8.2: Permeate Flux and Removal Percentage of Different Compounds during Diafiltration in the First Filtration Stage

EXP #	Used Membrane	Dia-Flux Range (kg /m^{2}h)	Added Dia-Volume (mL)	Removal (%)			
				Lignin	Organics Matters	Hemi-cellulose	Turbidity
1	**UC005**	65→ 59	350	54	22	17*	3
2	**UC005**	41→36	300	34	19	20*	8
		22→19	150				
3	**UC030**	119→ 112	250	23	39	48	-
		109→86	250				
		88→66	250				
4	**UC010**	140→131	300	52	36	24	13
		131→115	300				
		130→123	500				
5	**UC005**	92→ 86	500	23	28	37	-
		89→ 87	500				
6	**UC030**	137→ 128	500	39	62	64	11
		143→ 139	500				

: The removal % is for total carbohydrates

Table 8.3 : Permeate Flux and Removal Percentage of Different Compounds during Diafiltration in the Second Filtration Stage

EXP #	Used Membrane	Dia-Flux Range (Kg /m^{2}h)	Added Dia-Volume (mL)	Removal (%)			
				Lignin	Organic Matters	Hemi-cellulose	Turbidity
3	**GE-5**	14→11	250	15	13	5	36
4	**GE-10**	43→ 40	250	43	20	14	63
5	**GE-5**	32→24	500	36	18	6	72
	ETNA01PP	119→113	500	46	51	17	12
6	**ETNA01PP**	98→ 92	500	52	36	9	52

8.3 Separation Capability during Concentration of Hemicelluloses

During ultrafiltration high molar mass hemicelluloses (larger than membrane cut-off) are purified. Low molar mass soluble compounds pass through the membrane, while large molecules are retained during concentration. The selection of the membrane with proper cut-off was based on the average molar mass of the soluble hemicelluloses in the extraction liquor (provided by Metla Research Center).

Preliminary Experiments

During implementation of the preliminary filtration experiments liquors at different range of extraction temperature (see Appendix I) were processed in the dead end filtration unit. From the filtration sample analysis and retention calculations (see Appendices III, IV) the following points were observed:

- Most of the suspended solids were retained in the first filtration stage. While MF was effective to remove them from extraction solution (where the range of the extraction temperature was 70-134 ºC); UF was better to retain the most suspended solids from the extraction solution (where the range of the extraction temperature was 134 -155ºC).

- The highest separation capability of lignin from hemicelluloses from extraction solution (the range of the extraction temperature was 70-134 ºC) was achieved using the UC030 membrane ($R_{Hemicelluloses}/R_{Lignin} = 14$).

- The highest separation capability of lignin from hemicelluloses from extraction solution (the range of the extraction temperature was 134-155 ºC) was achieved using the UC005 membrane ($R_{Hemicelluloses}/R_{Lignin} = 3$). **The detailed results of different filtration samples analysis and retention values in preliminary experiments are shown in the appendices (III, IV).**

Main Filtration Experiments

The effect of the membrane cut-off on the hemicelluloses and other compounds retention during the first stage of filtration were studied. The retention calculations (based on equation # 5) showed that the retention of hemicelluloses and lignin using the UC005 membrane was higher than other UF membrane. However, most of the suspended solids were retained in the first filtration step.

In the second filtration stage the chemical nature of the membranes surface had significant effect on the retention of different compounds. The analysis results showed that the retention of different compounds by the GE-5 membrane was higher than the retention by the ETNA01PP membrane. The retention of hemicelluloses by the GE-5 membrane was the highest when its feed solution was the permeate of the UCO30 membrane (EXP# 3). The hemicelluloses retention by the GE-10 membrane (EXP# 4) was higher than by the GE-5 membrane when its feed solution was the UC005 membrane permeate (EXP# 5-b_1). The possible reason can be the difference in molar masses and fractions of hemicelluloses in the feed of those membranes where they come from the ultrafiltration membranes with different cut-off. Nevertheless, the highest total retention of lignin was achieved when the UC005→GE-5 membrane set was used. The UC030→ GE-5 membrane set was the best to concentrate hemicelluloses.

The selection of the suitable membrane to achieve high separation of lignin from hemicelluloses is based on the ratio between hemicelluloses and lignin retention. Higher ratio corresponds to better separation. In our filtration the GE-5 and ETNA01PP membranes showed potential to purify and separate lignin from hemicelluloses (EXPs# 3-b, 5-b_2).During the first filtration stage the UC005 membrane (lowest cut-off) had the higher separation of lignin from hemicelluloses (EXP# 5-a). The best set to separate lignin from hemicelluloses was the UC030→GE-5 membrane set (EXP# 3 a-b). Table 8.4 summarizes the retention values of lignin, hemicelluloses and other organics.

The retention of turbidity was usually high in the first and second filtration steps. The pH values were from 3.5-4.5. That means the extraction solutions were slightly acidic. The range of the conductivity values of filtration samples was 300-600 μS/cm that showed the concentration of ionic species in the feed solutions was relatively low. **The detailed results of different analysis measurements are shown in the appendix (V).**

Table 8.4: Retention Values during the First and Second Filtration Stages

EXP #	Step	Used Membrane	R Lignin (%)	R Organics (%)	R Hemi-cellulose (%)	R Turbidity (%)
1	a	UC005	25	36	43*	99
	b	GE-5	24	48	67*	50
		R_{Total} %	***44***	***67***	***81****	***100***
2	a	UC005	32	50	53*	91
	b	GE-5	34	46	55*	66
		R_{Total} %	***55***	***73***	***79****	***97***
3	a	UC030	19	24	18	87
	b	GE-5	44	74	96	98
		R_{Total} %	***55***	***80***	***97***	***100***
4	a	UC010	27	44	55	85
	b	GE-10	33	54	74	84
		R_{Total} %	***51***	***74***	***88***	***98***
5	a	UC005	31	41	77	97
	b1	GE-5	38	51	58	96
		R_{Total} %	***57***	***71***	***90***	***100***
	b2	ETNA01PP	3	25	52	97
		R_{Total} %	***39***	***60***	***74***	***100***
6	a	UC030	28	18	25	98
	b	ETNA01PP	15	21	30	_
		R_{Total} %	***38***	***36***	***48***	***97***

****: The retention % is for total carbohydrates.***

8.4 Separation of Monosaccharides from Spruce Hemicelluloses

Detailed analysis for the filtration samples were done by Finnish Forest Research Institute (Metla). The retention of primary spruce hemicelluloses (glucomannan and xylan) during different filtration sets could be calculated from this analysis data. The removal percentage of them could also be determined. Table 8.5 shows the retention values and removal percentage of those hemicelluloses.

Table 8.5 : Retention of Primary Spruce Hemicelluloses and Removal Percentage of them by Diafiltration during the First and Second Filtration Stage

EXP #	Step	Used Membrane	Retention (%)		Removal (%)	
			Glucomannan	Xylan	Glucomannan	Xylan
3	a	UC030	20	9	46	69
	b	GE-5	97	92	5	10
	R_{Total} %		***98***	***93***	-	-
4	a	UC010	59	32	20	57
	b	GE-10	81	59	12	18
	R_{Total} %		***92***	***72***	-	-
5	a	UC005	76	71	35	60
	b1	GE-5	74	25	6	4
	R_{Total} %		***94***	***78***	-	-
	b2	ETNA01PP	47	53	19	17
	R_{Total} %		***78***	***53***	-	-
6	a	UC030	28	17	63	78
	b	ETNA01PP	30	26	10	11
	R_{Total} %		***49***	***39***	-	-

From table 8.5 the following viewpoints can be observed:

- Ø The retention of glucomannan and xylan in the first filtration stage increases as the cut off of the membrane decreases. Membranes with lower cut-off showed a higher retention (Retention by UC005> UC010> UC030). In addition, the retention of glucomannan was higher than xylan retention in all first filtration stages.

- Ø The highest removal percentage of glucomannan in the first filtration stage was achieved by the UC030 membrane (EXP# 6-a) where the same volume of the diafiltration water was added as (EXP# 4-a, EXP# 5-a) when the UC010 and the UC005 membranes were used, respectively. The removal of this hemicellulose

from the UC005 membrane concentrate was higher than from the UC010 membrane concentrate. The same behavior can be observed in the case of xylan. Nevertheless, the removal of xylan by diafiltration was higher than glucomannan removal in all cases. The best separation of xylan from glucomannan by diafiltration was achieved using the UC010 membrane (xylan removal: glucomannan removal was 3:1)

- The retention of glucomannan was approximately complete in the second filtration stage by the GE-5 membrane when its feed solution was the permeate of the UC030 membrane. On the other hand, the retention of glucomannan by the GE-5 membrane was three times higher than xylan retention when its feed solution was the permeate of the UC005 membrane (EXP# 5-b_1)

- The removal of glucomannan and xylan during diafiltration in the second filtration stage was usually low. The removal of them from the GE-5 concentrate was the lowest (EXPs# 3-b, 5-b_1).

The separation efficiency of monomeric sugars from hemicelluloses can be defined using the separation factor (X_{mono}) (calculation based on equation # 8). This factor is a measure of monomeric sugars separation from hemicelluloses. The separation is achieved if the separation factor differs from one. A value greater than one indicates most of monomeric sugars passing through the membrane (monomeric sugars enrichment in the permeate).

High difference between the removal of hemicelluloses and monomeric sugars means better purification of hemicelluloses. Table 8.6 shows the retention of hemicelluloses and monomeric sugars and the separation factor of monomeric sugars. The removal of them by diafiltration is also shown.

Table 8.6: The Separation factor of Monomeric Sugars (X_{mono}) from Hemicelluloses and the Removal of Monomeric Sugars from Hemicelluloses during Diafiltration

EXP #	Step	Used Membrane	Retention (%)			Removal (%)	
			Hemi-celluloses	Monomer Sugars	X_{mono}	Hemi-celluloses	Monomer Sugars
3	a	UC030	18	-23	1.5	48	90
	b	GE-5	96	40	15.0	5	34
	R_{Total} %		***97***	***26***	***24.7***	**-**	**-**
4	a	UC010	55	6	2.1	24	94
	b	GE-10	74	14	3.3	14	49
	R_{Total} %		***88***	***20***	***6.7***	**-**	**-**
5	a	UC005	77	7	4.0	37	94
	b1	GE-5	58	10	2.1	6	55
	R_{Total} %		***90***	***16***	***8.4***	**-**	**-**
	b2	ETNA01PP	52	-8	2.3	17	53
	R_{Total} %		***74***	***-6***	***4.1***	**-**	**-**
6	a	UC030	25	3	1.3	64	94
	b	ETNA01PP	30	8	1.3	9	41
	R_{Total} %		***48***	***11***	***1.7***	**-**	**-**

From table 8.6 the following viewpoints can be observed:

- Ø The negative retention means the concentration of the monomeric sugars in the permeate is higher than in the feed.

- Ø According to values of the monomeric sugars separation factor the best separation of monomeric sugars from hemicelluloses in the first filtration stage was obtained by the UC005 membrane (EXP# 5-a). The separation by the UC010 membrane was slightly higher than by the UC030 membrane.

- Ø The best separation of monomeric sugars from hemicelluloses in the second filtration stage was obtained by the GE-5 membrane (EXP# 3-b) when its feed solution was the permeate of the UC030 membrane.

- Ø The best filtration set for the separation of monomeric sugars from hemicelluloses was UC030→GE-5 (EXP# 3) where the retention of hemicelluloses was approximately complete.

- The purification of hemicelluloses can be done by diafiltration. In this study the best purification of monomeric sugars from hemicelluloses was achieved by the GE-5 membrane ((EXP #5-b_1) when its feed solution was the permeate of the UC005 membrane.

- The best separation of monomeric sugars from hemicelluloses by diafiltration in the first filtration stage was achieved by the UC010 membrane where the volume of water added was the highest. The removal of monomeric sugars by diafiltration in the first filtration stage was usually high.

The lignin retention and removal by diafiltration was calculated for the experiments 3 and 4. The results showed that the relative partial separation of lignin from hemicelluloses can be achieved. The purification of hemicelluloses by diafiltration succeeded to remove part of the lignin from the membrane concentrate. Table 8.7 shows the retention and removal of the lignin by diafiltration. **The detailed data about hemicelluloses and monomeric sugars content, retention and removal is shown in appendix (VI).**

Table 8.7: Retention and Removal of lignin in Experiments 3 and 4

EXP #	Step	Used Membrane	Lignin	
			Retention (%)	Removal (%)
3	a	UC030	11	30
	b	GE-5	59	10
	R_{Total} %		64	-
4	a	UC010	30	14
	b	GE-10	40	29
	R_{Total} %		58	-

9. CONCLUSION

The separation of hemicelluloses from the pressurized hot water extraction liquor using ultrafiltration and tight ultrafiltration membranes was investigated in this study. The membrane cut-off and surface materials have the significant effect on the filtration performance. The permeate flux during concentration of the liquor decreased only slightly in the first and second filtration stage. Relatively low fouling effect was observed in the first filtration stage. The effect of fouling was usually higher in the second filtration stage especially when GE-5 membrane was used.

The purification of the retained hemicelluloses by diafiltration accomplished partial removal of lignin-related compounds. The removal of monosaccharides was usually high (especially in the ultrafiltration step). The separation of lignin and monosaccharides from the retained hemicelluloses depended on the amount of the added water during diafiltration. The UC030 membrane (highest cut-off) purified high molar masses hemicelluloses during the first filtration stage. In the second filtration stage, the GE-5 and ETNA01PP membranes showed potential to purify hemicelluloses from lignin while the GE-5 membrane was highly efficient to purify hemicelluloses from monosaccharide.

The membrane cut-off and material had the significant effect on the retention of hemicelluloses and purification of them by diafiltration. The membrane cut-off was the determinant factor in the first filtration step. Membrane with lower cut-off gave better retention. So the best separation of lignin and monosaccharides from hemicelluloses was obtained by the UC005 membrane (cut-off 5000 g/mol). The purification of hemicelluloses from lignin and monosaccharides during diafiltration by this membrane was also higher than other UF membranes. The GE-5 and ETNA01PP membranes showed potential to separate lignin from hemicelluloses. However, the origin of the feed solution of the second filtration stage (permeates from different UF membranes-first filtration stage) had high effect on the permeate flux, hemicelluloses retention and purification by diafiltration during this filtration stage.

Separation of the primary spruce hemicelluloses (glucomannan and xylan) can be possible. The retention of them was based on their molar mass. Large difference between glucomannan and xylan retention means good separation of those hemicelluloses. Difference in removal percentage by diafiltration means efficient purification. However, the best separation of degraded xylan from glucomannan was achieved by using the GE-5 membrane.

Finally, to provide more clear description and evaluation the performance of the filtration and purification of hemicelluloses using different UF and TUF membranes; detailed and specific analysis of the content of all streams is required. This analysis has to give enough information about molar masses, fraction of each compound, and behavior of soluble compounds in different filtration streams. This information is helpful to select proper membrane cut-off, material and suitable operating conditions of the filtration.

REFERENCES

1. Aspinall, G. 1959. Structural Chemistry of Hemicelluloses. *Advances in Carbohydrate Chemistry*, vol. 14, pages 429-468.

2. Timell, T. 1965. Wood Hemicelluloses II. *Advances in Carbohydrate Chemistry*, vol. 20, pages 409-483.

3. Jacobs, A., and Dahlman, O. 2001**.** Characterization of the Molar Masses of Hemicelluloses from Wood and Pulps Employing Size Exclusion Chromatography and Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry. *Biomacromolecules*, vol. 2, pages 894-905.

4. Sjostrom, E. 1993. Wood Chemistry Fundamentals and Applications**.** 2nd Edition, San Diego: Academic press.

5. Bikova, T., and Treimanis A. 2002. Solubility and Molecular Weight of Hemicelluloses from Alnus incana and Alnus glutinosa. Effect of Tree Age**.** *Plant Physiology and Biochemistry*, vol. 40, pages 347–353.

6. Teleman, A., Nordström, M., Tenkanen, M., Jacobs, A. and Dahlman, O. 2003. Isolation and Characterization of *O*-acetylated Glucomannans from Aspen and Birch Wood. *Carbohydrate Research*, vol. 338, pages 525–534.

7. Stenius, P. and. Len, R**.** 2000. Forest Products Chemistry**.** *Book 3 of Papermaking Science and Technology seri*es, pages 28-29.

8. Sun, R. and Tomkinson, J. 2000 .Fractionation and Characterization of Water-Soluble Hemicelluloses and Lignin from Steam-Exploded Birchwood. *International Journal of Polymeric Matter*, vol. 45, pages 1-19.

9. Willfor, S., Sundberg, K., Tenkanen, M. and Holmbom, B. 2008. Spruce Derived Mannans-A Potential Raw Material for Hydrocolloids and Novel Advanced Natural Materials. *Carbohydrate Polymer*, vol. 72, pages 197-210.

10. Cellulose & Hemicelluloses Group. Hemicellulose-Related Research**.** Federal Research Centre for Forestry and Forest Products (BFH) and Centre of Wood Science, University of Hamburg.

11. (http://en.wikipedia.org/wiki/Hemicellulose). 25/2/2008.

12. Holladay, J., Bozell**,** J., White, J. and Johnson, D. 2007. Top Value-Added Chemicals from Biomass. Pacific Northwest National Laboratory.

13. Gabrielii, I. and Gatenholm, P. 1998 .Preparation and Properties of Hydrogels Based on Hemicellulose**.** *Journal of Applied Polymer Science*, vol. 69, pages 1661–1667**.**

14. Gabrielii, I., Gatenholm, P., Glasser, W.G., Jain, R.K and. Kenne, L. 2000**.** Separation, Characterization and Hydrogel-Formation of Hemicellulose from Aspen Wood. *Carbohydrate Polymers*, vol. 43, pages 367–374.

15. Betts, W., Dart, R., .Ball, A. and Pedlar, S. 1992**.** Biosynthesis and Structure of Lignocellulose. In: Biodegradation. *Natural and Synthetic Materials*, pages 139-156.

16. Gonzalez, J., Cruz, J., Dominguez, H. and Parajo J. 2004. Production of Antioxidants from Eucalyptus Globulus Wood by Solvent Extraction of Hemicellulose Hydrolysates**.** *Food Industry*, vol. 84, pages 243-251.

17. Hansen, N. and Plackett, D. 2008. Sustainable Films and Coatings from Hemicelluloses: A Review. *Biomacromolecules,* vol. 9, pages 1493-1505**.**

18. Gurgel, P., Mancilha, I.., Pecanha, R. and Siqueira, J. 1995. Xylitol Recovery from Fermented Sugarcane Bagasse Hydrolyzate. *Bioresources Technology,* vol. 52, pages 219-223.

19. Krawczyk, H., Persson, T., Andersson, A. and Jönsson, A.-S. Isolation of Hemicelluloses from Barley Husks. 2008. *Food and Bioproducts Processing, pages* 31-36.

20. Palm, M. and Zacchi, G. 2003. Extraction of Hemicellulosic Oligosaccharides from Spruce Using Microwave Oven or Steam Treatment. *Biomacromolecules,* vol. 4, pages 617-623.

21. Agenda 2020 Technology Alliance and American Forest & Paper Association .2006. Forest Products Industry Technology Roadmap**.** U.S. Department of Energy and Office of Energy Efficiency and Renewable Energy Industrial Technologies Program.

22. Del, R. and Closet, G. 2004. Forest Products Biorefinery: Technology for a New Future. *Solutions for People, Processes and Paper*, vol. 87, pages 49-53.

23. Kenealy, W., Houtman, C., Laplaza, J., Jeffries, T. and Horn, E. 2007. Pretreatments for Converting Wood into Paper and Chemicals. *American Chemical Society*, pages 392-408.

24. Pisarnitskii, A., Rubeniya, T. and Rutitskii**,** A. 2006. Oak Wood Hemicelluloses Extracted with Aqueous–Alcoholic Media**.** *Applied Biochemistry and Microbiology,* vol. 42, pages 514-518.

25. Janzon, R., Saake, B. and Puls**,** J. 2008. Upgrading of Paper-Grade Pulps to Dissolving Pulps by Nitren Extraction: Properties of Nitren Extracted Xylans in Comparison to NaOH and KOH Extracted Xylans. *Cellulose*, vol. 15, pages 161–175.

26. Persson, T., Jönsson, A.-S. and Zacchi, G. 2005. Fractionation of Hemicelluloses by Membrane Filtration**.** 14th European Biomass Conference, pages 1693-1696.

27. Andersson, A., Persson, T., Zacchi, G., Stålbrand, H. and Jönsson, A. 2007. Comparison of Diafiltration and Size-Exclusion Chromatography to Recover Hemicelluloses from Process Water from Thermo-mechanical Pulping of Spruce. *Applied Biochemistry and Biotechnology*, pages 136–140.

28. Tsoumis, G. 1991. Science and Technology of Wood –Structure, Properties, Utilization. Van Nostrand Reinhold.

29. Laine, C. 2005. Structures of Hemicelluloses and Pectins in Wood and Pulp. Degree of Doctor of Science in Technology, Department of Chemical Technology, Helsinki University of Technology.

30. Hu, G., Heitmann, J. and Rojas, O. 2008. Feedstock Pretreatment Strategies for Producing Ethanol from Wood, Bark, and Forest Residues. *Bio-resources*, vol. 3, pages 270–294.

31. Gáspár, M., Kálmán, G. and Réczey, K. 2007. Corn Fiber as a Raw Material for Hemicellulose and Ethanol Production. *Process Biochemistry*, vol. 42, pages 1135–1139.

32. Geng, Z., Sun, R., Sun, X. and Lu, Q. 2003. Comparative Study of Hemicelluloses Released during Two-Stage Treatments with Acidic Organosolv and Alkaline Peroxide from Caligonum Monogoliacum and Tamarix Spp. *Polymer Degradation and Stability*, vol. 80, pages 315–325.

33. Sun, R., Fang, J., Tomkinson, J., Geng, Z. and Liu, J. 2001**.** Fractional Isolation, Physico-Chemical Characterization and Homogeneous Esterification of Hemicelluloses from Fast-Growing Poplar Wood. *Carbohydrate Polymers*, vol. 44, pages 29–39.

34. Rodriguez, J., Perez, M. and de Castro, L. 2003. Extraction of Wood Compounds by Use of Subcritical Fluids. *Chromatographia*, vol. 57, pages 363-368.

35. Curling, S., Fowler, P. and Hill, C. 2007**.** Development of a Method for the Production of Hemicellulosic Gels from Sitka Spruce. *Carbohydrate Polymers*, vol. 69, pages 673–677.

36. Garrote, G., Dominguez, H. and Parajo, J. 2001. Study on the Deacetylation of Hemicelluloses during the Hydrothermal Processing of Eucalyptus Wood. *Holz als Roh-und Werkstoff*, vol. 59, pages 53-59.

37. Shin, H-D., Le, T., Clarke, C. and Ruizhen Chen, R. 2006. Enzymatic Extraction of Wood Hemicellulose School of Chemical and Biomolecular Engineering, Georgia Institute of Technology.

38. Yu, Y., Lou, X. and Wu, H. 2008. Some Recent Advances in Hydrolysis of Biomass in Hot-Compressed Water and Its Comparisons with Other Hydrolysis Methods. *Energy and Fuels*, vol. 22, pages 46–60.

39. Mosier, N., Wyman, Ch., Dale, B., Elander, R., Lee, Y., Holtzapple, M. and Ladisch, M. 2005**.** Features of Promising Technologies for Pre-treatment of Lignocellulosic Biomass. *Bioresource Technology*. vol. 96, pages 673–686.

40. Cruz, J., Domı´nguez, J., Domı´nguez, H. and Parajo, J. 1999**.** Solvent Extraction of Hemicellulosic Wood Hydrolysates: a Procedure Useful for Obtaining Both Detoxified Fermentation Media and Polyphenols with Antioxidant Activity. *Food Chemistry*, vol. 67, pages 147–153.

41. Lee, Y., Iyer, P. and Torget, R. 1999. Dilute-Acid Hydrolysis of Lignocellulosic Biomass. *Advances in Biochemical Engineering and Biotechnology*, vol. 65, page 93.

42. Torget, R., Kidam, K., Hsu, T –A., Philippidis, G.P. and Wyman, C.E. 1998. Prehydrolysis of Lignocellulose. US Patent No. 5,705,369.

43. Örså, F., Holmbom, B. and Thornton, J. 1997. Dissolution and Dispersion of Spruce Wood Components into Hot Water. *Wood Science and Technology*, vol. 31, pages 279-290.

44. Wallberg, O., Linde, M. and Jönsson, A. 2006. Extraction of Lignin and Hemicelluloses from Kraft Black Liquor. *Desalination*, vol. 199, pages 413–414.

45. Ballerini, D., Desmarquest, J.P. and Pourquie, J. 1994. Ethanol Production from Lignocellulosic: Large Scale Experimentation and Economics. *Bioresourse Technology*, vol. 50, pages 17-23.

46. Amidon, T., Bolton, T., Francis, R. and Gratien, K. 2006. Effect of Hot Water Pre-Extraction on Alkaline Pulping of Hardwoods. TAPPI .Engineering, Pulping and Environmental Conference.

47. William, J., Frederick, JR., Steven, JL., Charles, A. and Kristiina, L. 2006. Ethanol Production from Hemicellulose Extracted from Southern Pine. School of Chemical & Bio-molecular Engineering, Georgia Institute of Technology.

48. Sundberg, A., Willför, S., Rehn, P. and Holmbom, B. 2003**.** Can Water-Soluble O-Acetyl-Galactoglucomannans be isolated in Large-Scale from TMP?. 2003. Proceedings 12th International Symposium on Wood and Pulping Chemistry, vol. 2, Madison: University of Wisconsin- Madison.

49. Hartman, J. 2006. Hemicellulose as Barrier Material**.** KTH Chemical and Science Engineering.

50. Hartonen, K. 1999. Supercritical Fluid Extraction and Pressurized Hot Water Extraction-Novel Environmentally Friendly Analytical Techniques. Department of Chemistry, University of Helsinki.

51. Kronholm, J., Hartonen, K. and Riekkola, M. 2007**.** Analytical Extractions with Water at Elevated Temperatures and Pressures. *Trends in Analytical Chemistry*, vol. 26.

52. Lüthje, K. 2004. On-line Coupling of Pressurised Hot Water Extraction and Microporous Membrane Liquid–Liquid Extraction with Chromatography in Analysis of Environmental Samples. Department of Chemistry, University of Helsinki.

53. Lüthje, K., Hyötyläinen, T. and Riekkola, M-L. 2004. Comparison of Different Trapping Methods for Pressurised Hot Water Extraction. *Journal of Chromatography A*, vol. 1025, pages 41–49.

54. Mok, W. and Antal, M. 1992**.** Uncatalyzed Solvolysis of Whole Biomass Hemicellulose by Hot Compressed Liquid Water. *Industrial Engineering Chemistry*, vol. 31, pages 1157-1161.

55. Bobleter, O. 1994. Hydrothermal Degradation of Polymers Derived from Plants. *Programming Polymer Science*, vol. 19, pages 797–841.

56. Wyman, C., Dale, B., Elander, R., Holtzapple, M., Ladisch, C. and Lee, Y. 2005**.** Coordinated Development of Leading Biomass Pre-treatment technologies**.** *Bio-resource Technology*, vol. 96, pages 1959–1966.

57. Van Heiningen, A., Tunc, M. and Macewan, K. 2005. Extraction of Hemicellulose from Mixed Southern Hardwood using Hot Water Extraction' AIChE Annual Meeting, Conference Proceedings, page 9527.

58. Jollez, P., Chornet, E. and Overend, R. 1994**.** Steam-Aqueous Fractionation of Sugar Cane Bagasse: An Optimization study of Process Conditions at the Pilot Plant Level. *Advances in Thermo-chemical Biomass Conversion*, vol. 2, page 1659.

59. Allen, S., Schulman, D., Lichwa, J. and Antal, M. 2001. A Comparison between Hot Liquid Water and Steam Fractionation of Corn Fiber. *Industrial Engineering Chemistry*, vol. 40, pages 2934-2941.

60. Lundqvist, J., Jacobs, A., Palm, M., Zacchi, G., Dahlman, O. and Sta°lbrand, H. 2003**.** Characterization of Galactoglucomannan Extracted from Spruce (Picea abies) by Heat-Fractionation at Different Conditions**.** *Carbohydrate Polymers*, vol. 51, pages 203–211.

61. Pèrez, J., González, A., Oliva, J., Ballesteros, I. and Manzanares, P. 2007. Effect of Process Variables on Liquid Hot Water Pretreatment of Wheat Straw for Bioconversion to Fuel-Ethanol in a Batch Reactor**.** *Journal of Chemical Technology and Biotechnology*, vol. 82, pages 929–938.

62. Hasegawa, I., Tabata, K., Okuma, O. and Mae, K. 2004. New Pre-treatment Methods Combining a Hot Water Treatment and Water/Acetone Extraction for

Thermo-Chemical Conversion of Biomass**.** *Energy and Fuels*. vol. 18, pages 755-760.

63. Palm, M. and Zacchi, G. 2004**.** Separation of Hemicellulosic Oligomers from Steam-Treated Spruce Wood Using Gel Filtration. *Separation and Purification Technology*, vol. 36, pages 191–201.

64. Karlsson, P., Roubroeks, J., Glasser, W. and Gatenholm, P. 2006. Optimization of the Process Conditions for the Extraction of Heteropolysaccharides from Birch (Betula pendula). *American Chemical Society*, pages 321-333.

65. Hartonen, K., Parshintsev, J., Sandberg, K. Bergelin, E., Nisula, L.and Riekkola, M-L. 2007. Isolation of Flavonoids from Aspen Knotwood by Pressurized Hot Water Extraction and Comparison with Other Extraction Techniques**.** *Talanta*, vol. 74, pages 32–38.

66. Buranov, A. and Mazza, G. 2007. Fractionation of Flax Shives by Water and Aqueous Ammonia Treatment in a Pressurized Low-Polarity Water Extractor. *Journal of Agricultural and Food Chemistry*, vol. 55, pages 8548–8555.

67. Liu, C. and Wyman, CE. 2005. Partial Flow of Compressed-Hot Water through Corn Stover to Enhance Hemicellulose Sugar Recovery and Enzymatic Digestibility of Cellulose. *Bioresource Technology*, vol. 96, pages 1978–1985.

68. Liu, C. and Wyman, CE. 2004. The Effect of Flow Rate of Very Dilute Sulfuric Acid on Xylan, Lignin, and Total Mass Removal from Corn Stover. *Industrial Engineering Chemistry*. vol. 86, pages 88–95.

69. Liu, C. and Wyman, CE. 2003. The Effect of Flow Rate of Compressed Hot Water on Xylan, Lignin, and Total Mass Removal from Corn Stover. *Industrial Engineering Chemistry*, vol. 42, pages 5409–5416.

70. Robinson, J., Keating, J.D., Mansfield, S.D. and Saddler**,** J.N. 2003. The Fermentability of Concentrated Softwood-Derived Hemicellulose Fractions with and without Supplemental Cellulose Hydrolysates. *Enzyme and Microbial Technology* , vol. 33, pages 757–765

71. Boussaid, A., Robinson J., Cai, J.Y., Gregg, DJ. and Saddler, JN. 1999 Fermentability of the Hemicellulose-Derived Sugars from Steam-Exploded Softwood**.** *Biotechnology Bioengineering*, vol. 64, pages 284–289.

72. Ando, H., Sakaki, T., Kokusho, T., Shibata, M., Uemura, Y. and Hatate, Y. 2000**.** Decomposition Behavior of Plant Biomass in Hot-Compressed Water. *Industrial Engineering Chemistry*, vol. 39, pages 3688-3693.

73. Mosier, N., Hendrickson, R., Ho, N., Sedlak, M. and Ladisch, R. 2005. Optimization of pH Controlled Liquid Hot Water Pre-treatment of Corn Stover. *Bioresource Technology*, vol. 96, pages 1986–1993.

74. Bertaud, F., Sundberg, A. and Holmbom, B. 2002. Evaluation of Acid Methanolysis for Analysis of Wood Hemicelluloses and Pectins**.** *Carbohydrate Polymers*, vol. 48, pages 319-324.

75. Lawther, J. Sun, R. and Banks, W. 1995. Extraction, Fractionation, and Characterization of Structural Polysaccharides from Wheat Straw**.** *Journal of Agricultural and Food Chemistry*. vol. 43, pages 667-675.

76. Huber, Ch., Grill, E., Oefner, P. and Bobleter, O. 1994. Capillary Electrophoretic Determination of the Component Monosaccharides in Hemicelluloses. *Fresenius Journal of Analytical Chemistry*, vol. 348, pages 825-831.

77. Mulder, M. 1996. Basic Principles of Membrane Technology**.** 2nd Edition, Kluwer Academic Publishers.

78. Gutman, R. 1987**.** Membrane Filtration –the Technology of Pressure – Driven Cross Flow Processes. IOP Publishing Ltd.

79. Rautenbach, R. and Albrecht, R. 1989. Membrane Processes. John Wiley & Sons Ltd.

80. Wagner, J. 2001. Membrane Filtration Handbook -Practical Tips and Hints. 2nd Edition, Osmonics.

81. Persson, T., Nordin, A-K., Zacchi, G. and Jönsson, A-S. 2007. Economic Evaluation of Isolation of Hemicelluloses from Process Streams from Thermo-mechanical Pulping of Spruce**.** *Applied Biochemistry and Biotechnology*, vol. 136-140, pages 741-752.

82. Turner, M.K. 1991. Effective Industrial Membrane Processes: Benefits and Opportunities. Elsevier Applied Science.

83. Alén, R., Sjöström, E. and Vaskikari, P. 1985**.** Carbon Dioxide Precipitation of Lignin from Alkaline Pulping Liquors. Cellulose Chemical Technology. vol. 19, pages 537–541.

84. Bhattacharya, P., Jayan, R. and Bhattacharjee, Ch. 2005**.** A Combined Biological and Membrane-Based Treatment of Pre-hydrolysis Liquor from Pulp Mill. *Separation and Purification Technology*, vol. 45, pages 119–130.

85. Nabarlatz, D., Torras, C., Valls, R–G. and Montan´e, D. 2007. Purification of Xylo-Oligosaccharides from Almond Shells by Ultrafiltration. S*eparation and Purification Technology*, vol. 53, pages 235–243.

86. Öhman, F. 2002. Precipitation and Separation of Lignin from Kraft Black Liquor. Doctoral thesis, Chalmers University of Technology-Sweden.

87. Wallberg, O., Holmqvist, A. and Jönsson, A-S. 2005. Ultrafiltration of Kraft Cooking Liquors from a Continuous Cooking Process. *Desalination*, vol. 180, pages 109-118.

88. Pizzichini, M., Russo, C. and Di Meo, C. 2005. Purification of Pulp and Paper Wastewater, with Membrane Technology, for Water Reuse in a Closed Loop. *Desalination*, vol. 178, pages 351-359.

89. Mänttäri, M., Nuortila-Jokinen, J. and Nyström, M. 1997. Evaluation of Nanofiltration Membranes for Filtration of Paper Mill Total Effluent. *Filtration and Separation*, pages 275- 280.

90. Nuortila-Jokinen, J., and Nyström, M. 1996. Comparison of Membrane Separation Processes in the Internal Purification of Paper Mill Water. *Journal of Membrane Science*, vol. 119, pages 99-115.

91. Persson, T., Matusiak, M., Zacchi, G. and Jönsson, A-S. 2006. Extraction of Hemicelluloses from Process Water from the Production of Masonite. *Desalination*, vol. 199, pages 411–412.

92. Andersson, A., Persson, T., Zacchi, G., Stålbrand**,** H. and. Jönsson, A.-S**.** 2007. Diafiltration and Gel Filtration – Two Methods for Purification of Hemicelluloses in Process Water from Thermo-Mechanical Pulping of Spruce. *Applied Biochemistry Biotechnology*, vol. 137-140, pages 971-983.

93. Schlesinger, R., Götzinger, G., Sixta, H., Friedl, A. and Harasek, M. 2006 Evaluation of Alkali Resistant Nanofiltration Membranes for the Separation of Hemicellulose from Concentrated Alkaline Process Liquors. *Desalination*, vol. 192, pages 303–314.

94. Sjöman, E., Mänttäri, M., Nyström, M., Koivikko, H. and Heikkilä, H. 2006. Nanofiltration of Monosaccharide Containing Solution to Recover Xylose**.** *Desalination*, vol. 199, pages 348–349.

95. Sjöman, E., Mänttäri, M., Nyström, M., Koivikko, H. and Heikkilä, H. 2008. Xylose Recovery by Nanofiltration from Different Hemicellulose Hydrolyzate Feeds. *Journal of Membrane Science*, vol. 310, pages 268–277.

96. Schlesinger, R., Röder, T., Götzinger, G., Sixta, H., Harasek, M. and Friedl, A. 2005. Influence of Hemicellulose Aggregate and Gel Layer Formation on Flux and Retention during Nanofiltration of Alkaline Solutions. *Desalination*, vol. 175, pages 121-134.

97. Yang, S., Ding, W. and Chen, H. 2006. Enzymatic Hydrolysis of Rice Straw in a Tubular Reactor Coupled with UF Membrane. *Process Biochemistry*, vol. 41, pages 721–725.

98. Freixo, M. and De Pinhob, M. 2002. Enzymatic Hydrolysis of Beech wood Xylan in a Membrane Reactor**.** *Desalination*, vol. 149, pages 237-242.

99. Han, B., Carvalho, W., Canilha, L., da Silva, S., Silva, J., McMillan, J. and Wickramasinghe S. 2006. Adsorptive Membranes vs. Resins for Acetic Acid Removal from Biomass Hydrolysates. *Desalination*, vol. 193, pages 361–366.

APPENDICES

A .Pre-experiments

Appendix I: Feed Solutions Fluxes

Appendix II: Fouling Effect

Appendix III: Turbidity, pH, and Conductivity Measurements

Appendix IV: Retention Calculations

B. Cross Flow Experiments

Appendix V: Samples Analysis and Retention Calculations

Appendix VI: Retention and Removal of Hemicelluloses, Monomeric Sugars and Lignin

A. Pre-experiments

The Millipore stirred cell (volume = 300 ml) was used to carry out the preliminary experiments. The average fluxes of feed solution through the used membranes, the fouling effect, and the retention of different compounds by different sets of membranes were measured as follow:

Appendix I: Feed Solutions Fluxes

The fraction of different wood hemicelluloses in the extraction liquor at different temperature is shown as follow:

Hemicelluloses (g/L)	**E. Solution at 70-134°C**	**E. Solution at 134-155°C**	**E. Solution at 155-169°C**	**E. Solution at 169-175°C**	**E. Solution at 175-180°C**
Arabinose	0.8	0.7	0.6	0.5	0.1
Rhamnose	0.1	0.1	0.1	0.1	0.0
Xylose	1.3	1.5	1.4	1.6	1.2
Mannose	4.0	4.2	4.0	4.5	2.6
Galactose	0.6	0.6	0.6	0.7	0.3
Glucose	1.1	1.1	1.0	1.1	0.7
Glucuronic Acid	0.1	0.0	0.0	0.0	0.0
Galacturonic Acid	0.4	0.4	0.3	0.2	0.1
4-O-Me Glucuronic Acid	0.2	0.2	0.2	0.1	0.0
C_{Total} (g/L)	***8.6***	***8.8***	***8.2***	***8.8***	***5.1***

(The data was taken from Finnish Forest Research Institute (Metla)).

The fraction of various monomeric sugars in the extraction liquor at different temperature is shown as follow:

Monomeric Sugars (g/L)	**E. Solution at 70-134°C**	**E. Solution at 134-155°C**	**E. Solution at 155-169°C**	**E. Solution at 169-175°C**	**E. Solution at 175-180°C**
Arabinose	0.8	0.7	0.5	0.1	0.0
Rhamnose	0.0	0.0	0.0	0.0	0.0
Xylose	0.2	0.2	0.5	0.7	0.4
Mannose	0.0	0.0	0.1	0.2	0.2
Fructose	0.2	0.0	0.0	0.0	0.0
Galactose	0.1	0.1	0.1	0.1	0.1
Glucose	0.1	0.0	0.0	0.1	0.0
Glucuronic Acid	0.0	0.0	0.0	0.0	0.0
Galacturonic Acid	0.3	0.3	0.3	0.2	0.1
C_{Total} (g/L)	***1.7***	***1.3***	***1.5***	***1.4***	***0.8***

(The data was taken from Finnish Forest Research Institute (Metla)).

The average permeates fluxes during filtration of the extraction liquor are shown as follow:

EXP SET	Membranes	Average Flux (kg/(m^2.h))	Pressure Range (bar)/ (Temperature) (ºC)	Original Feed Solution
1	**UC030**	22.0 - 28.0	1-3 (40 ºC)	Extraction solution at 70- 134 ºC
	UC010	60.5 - 82.1	2-4(40 ºC)	
	UC005	50.3 - 68.2	3-5 (40 ºC)	
2	**UC030**	32.5 – 35.0	2.5-3 (70 ºC)	Extraction solution at 70- 134 ºC
	UC010	82.0	3 (70 ºC)	
	UC005	56.4 – 70.3	3-4 (70 ºC)	
3	**MV020**	39.0 – 57.0	2-3 (40 ºC)	Extraction solution at 70- 134 ºC
	UC030	72.1 – 83.7	1-2 (70ºC)	
	UC010	75.5 - 85.3	2-3 (70 ºC)	
	UC005	60.6 – 77.9	3-4 (70 ºC)	
4	**MV020**	73.6 - 95.4	2-4 (70 ºC)	Extraction solution at 134 -155 ºC
	UC005	44.2 - 52.2	3 (70 ºC)	
5	**MV020**	75.6 - 95.1	2-3 (70 ºC)	Extraction solution at 134 -155 ºC
	UC030	48.0 - 58.1	1-2 (70 ºC)	
	UC005	62.0- 72.8	3-4 (70 ºC)	
6	**MV020**	60.0 – 71.0	1-2 (70 ºC)	Extraction solution at 155 -169 ºC
	UC005 Cross flow	52.0 – 90.0	2-4(70 ºC)	

Appendix II: Fouling Effect

The fouling and concentration polarization effect was detected by measuring pure water flux through the membrane before and after feed solution filtration. The pure water permeability (PWP) values are shown in the following table:

EXP SET	Membranes	PWP before Filtration (kg/(m^2.h.bar))	PWP after Filtration (kg/(m^2.h.bar))	% Fouling
1	**UC030**	223	182	18
	UC010	28	23	17
	UC005	26	16	40
2	**UC030**	323	261	19
	UC010	47	46	2
	UC005	28	19	33
3	**UC030**	362	264	27
	UC010	49	48	3
	UC005	28	19	33
4	**UC005**	29	15	47
5	**UC030**	362	264	27
6	**UC005**	31	25	20

Appendix III: Turbidity, pH, and Conductivity Measurements

The turbidity, pH and conductivity of the feed solution, permeate through the membrane and the concentrate from the membrane were also measured. The values of those measurements are shown in the following table:

EXP SET	Membrane	Sample	Turbidity (NTU)	$R_{Turbidity}$ (%)	pH	Conductivity (µS/cm)
1	UC030	Feed Solution	3935	96	3.93	615
		Permeate	179		3.97	596
		Concentrate	7460		3.89	644
	UC010	Feed Solution	179	27	3.97	596
		Permeate	130		4.0	525
		Concentrate	23		3.91	603
	UC005	Feed Solution	130	59	4.0	525
		Permeate	53		4.03	510
		Concentrate	133		3.96	642
2	UC030	Feed Solution	1523	90	3.92	699
		Permeate	150		3.93	696
		Concentrate	3394		3.81	837
	UC010	Feed Solution	150	66	3.93	696
		Permeate	51		3.96	695
		Concentrate	371		3.94	751
	UC005	Feed Solution	51	35	3.96	695
		Permeate	33		4.06	608
		Concentrate	233		3.97	580
3	MV020	Feed Solution	1496	94	3.92	656
		Permeate	89		4.08	648
		Concentrate	3192		3.97	562
	UC030	Feed Solution	89	55	4.08	648
		Permeate	40		4.09	590
		Concentrate	379		4.03	580
	UC010	Feed Solution	40	37	4.09	590
		Permeate	25		4.13	485
		Concentrate	198		4.02	593
	UC005	Feed Solution	25	49	4.13	485
		Permeate	13		4.15	522
		Concentrate	133		4.06	611
4	MV020	Feed Solution	3616	46	3.60	550
		Permeate	1942		3.60	606
		Concentrate	7586		3.55	617
	UC005	Feed Solution	1942	83	3.60	606
		Permeate	323		3.62	629
		Concentrate	955		3.49	682

5	**MV020**	Feed Solution	3616	66	3.60	550
		Permeate	1235		3.59	604
		Concentrate	4010		3.51	648
	UC030	Feed Solution	1235	90	3.59	604
		Permeate	118		3.59	593
		Concentrate after Di	3532		3.67	159
		Permeate of Di_1	12		3.71	276
		Permeate of Di_2	8		3.86	120
	UC005	Feed Solution	118	53	3.59	593
		Permeate	55		3.60	586
		Concentrate	785		3.49	635
6	**MV020**	Feed Solution	1127	66	3.63	650
		Permeate	388		3.59	617
		Concentrate	2786		3.51	642
	UC005* (Cross flow)	Feed Solution	388	5	3.60	617
		Permeate	369		3.62	608
		Concentrate	2003		3.49	652

Appendix IV: Retention Calculations

The total organic carbon content (TOC), total sugar content and the UV absorbent (at wave length around 280 nm) of the samples from different streams (feed, permeate, and concentrate) were measured. The retention of different compounds by the membrane can be calculated from those measurements. The following table shows the measurement values and the retention by different sets of membrane.

EXP SET	Membrane	Sample	TOC (ppm)	R_{TOC} (%)	UV Abs	R_{Abs} (%)	Carbo-hydrates (ppm)	R_{carbo} (%)
1	**UC030**	Feed Solution	5783	23	50.0	7	5063	19
		Permeate	4453		46.3		4120	
		Concentrate	15667		133.1		13025	
	UC010	Feed Solution	4453	33	46.3	20	4120	47
		Permeate	2971		37.1		2181	
		Concentrate	8203		51.4		7013	
	UC005	Feed Solution	2971	11	37.1	7	2181	18
		Permeate	2638		34.6		1790	
		Concentrate	5260		42.9		3700	
Overall Retention (%)			**54**		**31**		**65**	
2	**UC030**	Feed Solution	6037	36	53.9	11	4925	39
		Permeate	3889		48.0		3000	
		Concentrate	26658		174.1		19850	
	UC010	Feed Solution	3889	32	48.0	9	3000	11
		Permeate	2657		43.8		2670	
		Concentrate	4928		55.9		3775	
	UC005	Feed Solution	2657	3	43.8	19	2670	41
		Permeate	2566		35.5		1580	
		Concentrate	4252		50.6		3100	
Overall Retention (%)			**58**		**34**		**68**	
3	**MV020**	Feed Solution	6012	40	49.8	35	5513	45
		Permeate	3629		32.6		3050	
		Concentrate	10390		148.5		9450	
	UC030	Feed Solution	3629	9	32.6	2	3050	21
		Permeate	3317		32.1		2400	
		Concentrate	5702		40.1		6125	
	UC010	Feed Solution	3317	12	32.1	6	2400	11
		Permeate	2920		30.3		2140	
		Concentrate	5464		39.0		5700	
	UC005	Feed Solution	2920	15	30.3	3	2140	11
		Permeate	2479		29.4		1900	
		Concentrate	4953		37.1		4688	
Overall Retention (%)			**59**		**41**		**66**	

4	**MV020**	Feed Solution	7184	11	50.1	6	5513	15
		Permeate	6433		47.0		4700	
		Concentrate	11130		123.1		5675	
	UC005	Feed Solution	6433	39	47.0	16	4700	55
		Permeate	3911		39.6		2120	
		Concentrate	21701		88.1		19075	
Overall Retention (%)			**46**		**21**		**62**	
5	**MV020**	Feed Solution	5755	13	53.7	11	4288	14
		Permeate	5012		41.8		3675	
		Concentrate	15757		191.8		14180	
	UC030	Feed Solution	5012	3	41.8	4	3675	10
		Permeate	4869		40.0		3320	
		Diafiltration Concentrate	3779		11.3		3330	
		Permeate of Di_1	2545		15.3		2070	
		Permeate of Di_2	1239		5.22		1185	
	UC005	Feed Solution	4869	40	40.0	19	3320	52
		Permeate	2940		32.6		1610	
		Concentrate	14632		54.2		11675	
Overall Retention (%)			**49**		**39**		**62**	
6	**MV020**	Feed Solution	7084	7	64.5	23	5870	17
		Permeate	6607		50.0		4850	
		Concentrate	9928		184.3		7780	
	UC005* (Cross flow)	Feed Solution	6607	41	50.0	14	4850	46
		Permeate	3926		43.2		2610	
		Concentrate	18595		144.9		17080	
Overall Retention (%)			**45**		**33**		**56**	

B. Cross Flow Experiments

Appendix V: Samples Analysis and Retention Calculations

The total organic carbon content (TOC), total sugar content and the UV absorbent (at wave length around 280 nm) of the samples from different streams (feed, permeate, and concentrate) were measured. The retention of different compounds by the membrane can be calculated from those measurements. The turbidity, pH and conductivity of the feed solution, permeate through the membrane and the concentrate from the membrane were also measured. The following table shows the measurement values and the retention by different sets of membrane:

R: Retention

F: Feed Sample

P: Permeate Sample

C: Concentrate Sample

Di: Diafiltration

b: before Diafiltration

a: after Diafiltration

F_{1a} = Feed sample of experiment # 1, Step a

Re: Removal

RT: Total Retention

EXP Details	Sample Code	UV Abs	TOC (ppm)	Carbo-hydrates (ppm)	Turbidity (NTU)	pH	Conduct-ivity (µS/cm)
EXP #1	**F_{1a}**	44.0	2884	3520	2075	4.12	605
	P_{1a}	32.8	1855	2000	14	4.15	592
STEP a	**$C_{1a}b$**	68.8	6078	8950	6670	3.95	633
	$C_{1a}a$	30.3	4547	7120	6470	3.92	512
UC005	**$P_{1a}Di$**	10.4	890	920	6	4.8	258
Membrane	***R%***	***25***	***36***	***43***	***99***	**-**	***2***
EXP #1	**$F_{1b=}\ P_{1a}$**	32.8	1855	2000	14	4.15	592
	P_{1b}	24.8	957	655	7	4.15	510
STEP b	**C_{1b}**	42.1	4529	5190	156	3.98	624
GE-5	***R%***	***24***	***48***	***67***	***50***	**-**	***14***
Membrane	***R_{Total} %***	***44***	***67***	***81***	***100***		***16***
	F_{2a}	42.9	4478	5800	2670	3.88	612
EXP #2	**P_{2a}**	29.2	2243	2725	233	3.91	589
	$C_{2a}b$	112.0	12760	14420	8650	3.9	645
STEP a	**$C_{2a}a$**	71.2	9937	11200	7998	3.88	564
	$P_{2a}Di_1$	15.6	2211	2095	70	4.55	218
UC005	**$P_{2a}Di_2$**	9.2	1313	1270	30	4.6	188
Membrane	**$P_{2a}Di_3$**	12.7	1309	1125	13	4.63	153
	R%	***32***	***50***	***53***	***91***	**-**	***4***
EXP #2	**$F_{2b=}\ P_{2a}$**	29.2	2243	2725	233	3.91	589
	P_{2b}	19.3	1212	1225	79	3.87	521
STEP b	**C_{2b}**	42.7	5529	5360	493	3.92	599
GE-5	***R%***	***34***	***46***	***55***	***66***	**-**	***12***
Membrane	***R_{Total} %***	***55***	***73***	***79***	***97***		***15***
	F_{3a}	34.0	4392	3950	2217	4.22	388
EXP #3	**P_{3a}**	27.7	3351	2340	282	4.16	375
	$C_{3a}b$	55.3	7361	7880	3222	4.08	329
STEP a	**$C_{3a}a$**	42.5	4482	5320	3922	3.87	312
	$P_{3a}Di_1$	17.9	2483	2405	33	4.4	159
UC030	**$P_{3a}Di_2$**	10.5	1578	1690	5	4.72	143
Membrane	**$P_{3a}Di_3$**	5.7	1019	1170	2	4.88	112
	R%	***19***	***24***	***41***	***87***	**-**	***3***
	$F_{3b=}\ P_{3a}$	27.7	3351	2340	282	4.16	375
EXP #3	**P_{3b}**	15.4	878	1040	5	4.54	318
	$C_{3b}b$	45.7	7333	10500	389	3.92	355
STEP b	**$C_{3b}a$**	35.9	5919	8450	248	3.82	311
GE-5	**$P_{3b}Di$**	12.8	818	985	2	4.62	125
Membrane	***R%***	***44***	***74***	***56***	***98***	**-**	***15***
	R_{Total} %	***55***	***80***	***74***	***100***		***18***

EXP #4 STEP a UC010 Membrane	**F_{4a}**	32.8	4214	4625	1099	4.25	395
	P_{4a}	23.9	2375	2590	164	4.12	383
	$C_{4a}b$	42.3	7614	8515	2632	4	322
	$C_{4a}a$	19.6	4662	4300	2597	3.89	308
	$P_{4a}Di_1$	16.1	1805	1660	140	4.47	179
	$P_{4a}Di_2$	9.8	1103	1305	47	4.79	149
	$P_{4a}Di_3$	6.2	937.4	985	7	4.95	132
	R%	**27**	**44**	**44**	**85**	**-**	***3***
EXP #4 STEP b GE-10 Membrane	**$F_{4b=}$ P_{4a}**	23.9	2375	2590	164	4.21	383
	P_{4b}	16.0	1086	785	27	4.61	330
	$C_{4b}b$	29.1	4536	6130	103	3.87	361
	$C_{4b}a$	16.6	3619	5210	38	3.72	332
	$P_{4b}Di$	11.3	833.4	625	4	4.71	134
	R%	***33***	***54***	***70***	***84***	**-**	***14***
	R_{Total} %	***51***	***74***	***83***	***98***		***17***
EXP #5 STEP a UC005 Membrane	**F_{5a}**	39.5	3848	4530	1769	4.18	355
	P_{5a}	27.2	2290	2990	56	4.21	336
	$C_{5a}b$	131.6	13415	13770	8026	4.06	419
	$C_{5a}a$	99.9	9501	7350	8284	3.91	392
	$P_{5a}Di_1$	15.2	2123	2250	54	4.63	179
	$P_{5a}Di_2$	6.9	937	1100	18	4.88	146
	R%	***31***	***41***	***34***	***97***	**-**	***5***
EXP #5 STEP b1 GE-5 Membrane	**$F_{5b1=}$ P_{5a}**	27.2	2290	2990	56	4.23	336
	P_{5b1}	16.8	1121	865	2	4.72	284
	$C_{5b1}b$	40.5	4999	6238	238	3.81	401
	$C_{5b1}a$	24.7	3859	5088	67	3.66	382
	$P_{5b1}Di$	9.0	615	710	1	4.74	177
	R%	***38***	***51***	***71***	***96***	**-**	***16***
	R_{Total} %	***57***	***71***	***81***	***100***		***20***
EXP #5 STEP b2 ETNA01PP Membrane	**F_{org}**	43.6	4906	4767	2503	4.11	369
	F_{5b2}	26.5	2602	2480	27	4.17	345
	P_{5b2}	25.8	1951	2010	1	4.63	274
	$C_{5b2}b$	32.5	3125	3375	24	3.92	414
	$C_{5b2}a$	17.1	1484	1990	21	3.32	378
	$P_{5b2}Di$	10.7	916	1015	0	4.71	192
	R%	***3***	***25***	***19***	***97***	**-**	***21***
	R_{Total} %	***39***	***60***	***58***	***100***		***25***

EXP #6 **STEP a** **UC030 Membrane**	**F_{6a}**	37.2	3927	4820	1824	4.26	380
	P_{6a}	26.9	3212	3390	44	4.22	366
	C_{6a}b	69.7	5840	7125	5206	4.12	335
	C_{6a}a	42.9	2243	2838	4652	3.92	302
	$P_{6a}Di_1$	12.0	1485	1475	13	4.52	186
	$P_{6a}Di_2$	5.2	733.4	720	4	4.92	132
	R%	***28***	***18***	***30***	***98***	**-**	***4***
EXP #6 **STEP b** **ETNA01PP Membrane**	**$F_{6b=}$ P_{6a}**	26.9	3212	3390	44	4.22	366
	P_{6b}	22.9	2527	2250	47	4.55	265
	C_{6b}b	32.8	3674	4800	29	3.96	414
	C_{6b}a	15.9	2339	3075	14	3.54	373
	P_{6b}Di	10.0	903	940	1	4.86	183
	R%	***15***	***21***	***34***	**_**	**-**	***28***
	R_{Total} %	***38***	***36***	***53***	***97***		***30***

Appendix VI: Retention and Removal of Hemicelluloses, Monomeric Sugars and Lignin

The content of various hemicelluloses and monomeric sugars in feed, permeate and concentrate samples was determined by methanolysis-gas chromatography methods.

Galactoglucomannan and xylan were the main hemicelluloses in the samples. The following tables show the content, removal by diafiltration and retention of hemicelluloses and monomeric sugars.

Sugars Symbols

Mannose: Man

Glucose: Glc

Galactose: Gal

Arabinose: Ara

Xylose: Xyl

Rhamnose: Rha

Glucuronic Acid: GlcA

Galacturonic Acid: GalA

O-Me Glucuronic Acid: 4-O-Me-GlcA

Fructose: Fru

Main abbreviation

R: Retention

F: Feed Sample

P: Permeate Sample

C: Concentrate Sample

Di: Diafiltration

b: before Diafiltration

a: after Diafiltration

F_{3a} = Feed sample of experiment # 3, Step a

Re: Removal

RT: Total Retention

EXP#3:UC030 (a) →GE-5(b)

Ø Hemicelluloses Contents, Retention and Removal

Sample	Man	Glc	Gal	Ara	Xyl	Rha	GlcA	GalA	4-O-Me-GlcA	Total
F_{3a}	3475	842	357	24	825	27	21	186	39	5795
P_{3a}	2793	681	282	37	752	19	23	152	42	4781
R%	***20***	***19***	***21***	***-59***	***9***	***31***	***-11***	***18***	***-9***	***18***
C_{3a}b	6683	1635	652	87	1100	54	39	372	52	10623
C_{3a}a	3612	899	350	50	340	48	9	238	17	5545
Re %	***46***	***45***	***46***	***43***	***69***	***12***	***78***	***36***	***67***	***48***
P_{3a}Di	1558	373	151	23	339	14	7	77	15	2541
P_{3b}	80	18	1	0	61	0	6	23	8	144
R%	***97***	***97***	***100***	***100***	***92***	***100***	***72***	***85***	***81***	***97***
C_{3b}b	5624	1372	633	78	1667	45	29	295	75	9744
C_{3b}a	4989	1204	558	51	1377	41	24	257	63	8500
Re %	***4***	***5***	***4***	***27***	***10***	***3***	***12***	***6***	***8***	***5***
P_{3b}Di	133	40	20	-	128	-	6	23	9	334
RT%	***98***	***98***	***100***	***100***	***93***	***100***	***69***	***88***	***80***	***98***

Ø Monomeric Sugars Contents, Retention and Removal

Sample	Man	Glc	Gal	Ara	Xyl	Rha	Glc A	Gal A	Fru	Total
F_{3a}	122	47	111	302	336	23	0	0	33	974
P_{3a}	135	61	150	322	475	25	0	6	28	1202
R%	***-11***	***-31***	***-35***	***-7***	***-41***	***-8***	***-***	***-***	***16***	***-23***
C_{3a}b	112	42	103	274	316	22	0	0	31	899
C_{3a}a	11	2	13	33	33	1	0	0	0	93
Re %	***90***	***94***	***88***	***88***	***89***	***94***	***-***	***-***	***100***	***90***
P_{3a}Di	33	8	35	88	97	7	0	0	0	268
P_{3b}	80	17	85	241	252	20	2	6	15	717
R%	***41***	***73***	***43***	***25***	***47***	***22***	***-***	***-6***	***45***	***40***
C_{3b}b	169	68	156	378	441	31	0	0	53	1296
C_{3b}a	96	25	103	232	261	20	0	6	22	765
Re %	***36***	***56***	***26***	***31***	***33***	***27***	***-***	***-***	***51***	***34***
P_{3b}Di	70	15	77	198	205	17	2	6	15	606
RT%	***35***	***64***	***23***	***20***	***25***	***16***	***-***	***-***	***54***	***26***

Ø *Lignin Contents, Retention and Removal*

Sample	Lignin Concentration (ppm)	
F_{3a}	949	***R% = 11***
P_{3a}	840	
$C_{3a}b$	2202	***Re% = 30***
$C_{3a}a$	1541	
$P_{3a}Di$	346	***R% = 59***
P_{3b}	342	
$C_{3b}b$	1414	***Re% = 10***
$C_{3b}a$	1267	
$P_{3b}Di$	342	***RT% = 64***

Ø *Hemicelluloses Percentage (Hemicelluloses/Total Sugar)*

Sample	Man	Glc	Gal	Ara	Xyl	Rha	GlcA	GalA	4-O-Me-GlcA	Total
F_{3a}	97	95	76	7	71	54	100	100	100	86
P_{3a}	95	92	65	10	61	43	100	96	100	80
$C_{3a}b$	98	98	86	24	78	71	100	100	100	92
$C_{3a}a$	100	100	97	60	91	97	100	100	100	98
$P_{3a}Di$	98	98	81	21	78	67	100	100	100	90
P_{3b}	50	52	1	-	19	-	75	78	100	17
$C_{3b}b$	97	95	80	17	79	59	100	100	100	88
$C_{3b}a$	98	98	84	18	84	66	100	98	100	91
$P_{3b}Di$	65	73	21	-	38	-	75	80	100	36

EXP#4:UC010 (a) →GE-10(b)

Ø Hemicelluloses Contents, Retention and Removal

Sample	Man	Glc	Gal	Ara	Xyl	Rha	GlcA	GalA	4-O-Me-GlcA	Total
F_{4a}	3591	881	385	65	885	41	23	187	44	6102
P_{4a}	1457	360	197	15	601	15	16	86	25	2772
R%	***59***	***59***	***49***	***77***	***32***	***64***	***31***	***54***	***43***	***55***
C_{4a}b	7369	1821	697	102	1248	67	29	383	65	11716
C_{4a}a	5687	1411	481	78	514	63	22	308	29	8564
Re %	***20***	***20***	***29***	***21***	***57***	***3***	***21***	***17***	***53***	***24***
P_{4a}Di	1078	264	126	31	327	10	9	61	13	1906
P_{4b}	282	68	53	30	248	5	5	37	13	727
R%	***81***	***81***	***73***	***-99***	***59***	***68***	***69***	***57***	***49***	***74***
C_{4b}b	3647	895	490	82	1374	42	28	196	51	6754
C_{4b}a	3219	785	411	77	1129	38	8	161	26	5826
Re %	***12***	***12***	***16***	***7***	***18***	***8***	***72***	***18***	***50***	***14***
P_{4b}Di	163	36	5	-	68	-	0	14	5	233
RT%	***92***	***92***	***86***	***54***	***72***	***88***	***79***	***80***	***71***	***88***

Ø Monomeric Sugar Contents, Retention and Removal

Sample	Man	Glc	Gal	Ara	Xyl	Rha	Glc A	Gal A	Fru	Total
F_{4a}	126	49	114	303	344	23	0	11	34	1003
P_{4a}	117	45	107	289	323	22	0	1	35	938
R%	***7***	***8***	***6***	***5***	***6***	***4***	***-***	***91***	***-2***	***6***
C_{4a}b	123	48	112	294	329	22	0	2	33	964
C_{4a}a	7	0	7	20	20	0	0	0	0	53
Re %	***94***	***100***	***94***	***93***	***94***	***100***	***-***	***100***	***100***	***94***
P_{4a}Di	43	17	40	103	117	8	0	0	12	340
P_{4b}	98	31	95	254	282	18	0	0	26	804
R%	***16***	***32***	***11***	***12***	***13***	***17***	***-***	***100***	***25***	***14***
C_{4b}b	139	55	130	316	365	26	0	7	45	1084
C_{4b}a	73	26	72	161	188	13	0	3	19	555
Re %	***48***	***54***	***44***	***49***	***48***	***50***	***-***	***64***	***58***	***49***
P_{4b}Di	62	20	66	154	177	13	1	4	18	514
RT%	***22***	***37***	***16***	***16***	***18***	***21***	***-***	***100***	***23***	***20***

Ø *Lignin Contents, Retention and Removal*

Sample	Lignin Concentration (ppm)	
F_{4a}	1008	***R% = 30***
P_{4a}	708	
$C_{4a}b$	1482	***Re% = 14***
$C_{4a}a$	1278	
$P_{4a}Di$	318	***R% = 40***
P_{4b}	425	
$C_{4b}b$	981	***Re% = 29***
$C_{4b}a$	694	
$P_{4b}Di$	-	***RT% = 58***

Ø *Hemicelluloses Percentage (Hemicelluloses/Total Sugar)*

Sample	Man	Glc	Gal	Ara	Xyl	Rha	GlcA	GalA	4-O-Me-GlcA	Total
F_{4a}	97	95	77	18	72	64	100	94	100	86
P_{4a}	93	89	65	5	65	40	100	99	100	75
$C_{4a}b$	98	97	86	26	79	75	100	100	100	92
$C_{4a}a$	100	100	99	80	96	100	100	100	100	99
$P_{4a}Di$	96	94	76	23	74	56	100	100	100	85
P_{4b}	74	69	36	11	47	21	100	100	100	48
$C_{4b}b$	96	94	79	21	79	61	100	97	100	86
$C_{4b}a$	98	97	85	32	86	74	100	98	100	91
$P_{4b}Di$	72	64	7	-	28	-	-	77	92	32

EXP#5:UC005 (a) →GE-5(b1)/ETNA01PP (b2)

Ø *Hemicelluloses Contents, Retention and Removal*

Sample	Man	Glc	Gal	Ara	Xyl	Rha	GlcA	GalA	4-O-Me-GlcA	Total
F_{5a}	3660	951	413	64	912	42	24	217	55	6339
P_{5a}	881	232	89	0	266	3	7	65	28	1463
R%	***76***	***76***	***78***	***100***	***71***	***92***	***72***	***70***	***49***	***77***
C_{5a}b	15678	4104	1473	247	2110	139	46	831	97	24629
C_{5a}a	9872	2688	915	164	840	104	35	563	45	15181
Re %	***36***	***33***	***37***	***32***	***60***	***24***	***22***	***31***	***53***	***37***
P_{5a}Di	1642	431	176	57	393	15	22	83	14	2819
P_{5b1}	237	60	47	23	201	2	5	32	13	608
R%	***73***	***74***	***47***	***100***	***25***	***43***	***19***	***50***	***53***	***58***
C_{5b1}b	3723	1000	547	80	1539	55	11	217	81	7172
C_{5b1}a	4187	1099	581	135	1677	56	0	243	85	7977
Re %	***-***	***-***	***-***	***-***	***-***	***-***	***100***	***-***	***-***	***-***
P_{5b1}Di	235	63	46	13	170	5	4	17	11	552
RT%	***94***	***94***	***89***	***64***	***78***	***96***	***78***	***85***	***76***	***90***
F_{5b2}	1559	396	249	85	908	30	0	129	56	3381
P_{5b2}	817	220	124	0	426	8	0	74	42	1628
R%	***48***	***45***	***50***	***100***	***53***	***73***	***-***	***42***	***25***	***52***
C_{5b2}b	1757	441	255	18	919	34	20	143	67	3587
C_{5b2}a	1378	351	206	62	745	27	21	121	45	2911
Re %	***19***	***18***	***17***	***-***	***17***	***18***	***-***	***12***	***30***	***17***
P_{5b2}Di	474	130	81	35	268	7	7	41	5	1048
R_T%	***78***	***77***	***70***	***100***	***53***	***81***	***100***	***66***	***24***	***74***

Ø *Monomeric Sugar Contents, Retention and Removal*

Sample	Man	Glc	Gal	Ara	Xyl	Rha	GlcA	GalA	Fru	Total
F_{5a}	118	42	111	297	362	23	0	0	32	986
P_{5a}	113	34	111	300	313	23	0	0	27	922
R%	***4***	***20***	***0***	***-1***	***14***	***0***			***15***	***7***
C_{5a}b	122	46	121	297	353	19	0	0	0	958
C_{5a}a	5	0	6	26	20	0	0	0	0	57
Re %	***96***	***100***	***95***	***91***	***94***	***100***				***94***
P_{5a}Di	29	10	28	72	79	6	0	0	7	229
P_{5b1}	99	38	91	264	293	18	0	0	27	829
R%	***13***	***-12***	***18***	***12***	***6***	***21***			***3***	***10***
C_{5b1}b	162	63	154	382	436	31	0	17	58	1302
C_{5b1}a	76	31	72	160	189	14	0	0	21	562
Re %	***51***	***49***	***51***	***56***	***55***	***54***		***100***	***62***	***55***
P_{5b1}Di	48	11	48	126	141	10	0	5	15	405
RT%	***16***	***10***	***18***	***11***	***19***	***21***			***17***	***16***
F_{5b2}	90	41	102	382	305	20	0	4	31	974
P_{5b2}	93	44	109	415	329	22	0	4	33	1049
R%	***-4***	***-8***	***-8***	***-9***	***-8***	***-9***		***-8***	***-6***	***-8***
C_{5b2}b	111	49	128	465	371	26	0	13	40	1202
C_{5b2}a	52	22	60	213	166	11	0	3	19	546
Re %	***51***	***53***	***52***	***53***	***54***	***57***		***71***	***52***	***53***
P_{5b2}Di	34	16	38	149	118	8	0	0	10	373
R_T%	***21***	***-4***	***2***	***-40***	***9***	***6***			***-1***	***-6***

Ø *Hemicelluloses Percentage (Hemicelluloses/Total Sugar)*

Sample	Man	Glc	Gal	Ara	Xyl	Rha	GlcA	GalA	4-O-Me-GlcA	Total
F_{5a}	97	96	79	18	72	64	100	100	100	87
P_{5a}	89	87	45	-	46	12	100	100	100	62
C_{5a}b	99	99	92	45	86	88	100	100	100	96
C_{5a}a	100	100	99	86	98	100	100	100	100	99
P_{5a}Di	98	98	86	44	83	72	100	100	100	92
P_{5b1}	71	61	34	8	41	9	100	100	100	43
C_{5b1}b	96	94	78	17	78	64	100	93	100	84
C_{5b1}a	98	97	89	46	90	80	-	100	100	93
P_{5b1}Di	83	85	49	9	55	32	100	77	100	58
F_{5b2}	95	91	71	18	75	60	-	97	100	78
P_{5b2}	90	83	53	-	56	27	-	95	101	61
C_{5b2}b	94	90	67	4	71	56	100	92	100	74
C_{5b2}a	96	94	77	23	82	71	100	97	100	84
P_{5b2}Di	93	89	68	19	69	49	100	100	32	74

EXP#6:UC030 (a) →ETNA01PP (b)

Ø *Hemicelluloses Contents, Retention and Removal*

Sample	Man	Glc	Gal	Ara	Xyl	Rha	GlcA	GalA	4-O-Me-GlcA	Total
F_{6a}	3778	951	425	96	966	42	21	209	72	6559
P_{6a}	2776	689	323	64	800	31	20	160	54	4918
R%	***27***	***28***	***24***	***34***	***17***	***27***	***4***	***23***	***24***	***25***
C_{6a}b	5902	1514	608	108	1057	63	25	330	70	9676
C_{6a}a	2142	581	243	60	238	36	10	178	0	3488
Re %	***64***	***62***	***60***	***44***	***78***	***43***	***59***	***46***	***100***	***64***
P_{6a}Di	1185	296	118	36	243	8	15	52	15	1953
P_{6b}	1925	490	241	37	590	13	20	110	50	3426
R%	***31***	***29***	***25***	***42***	***26***	***58***	***2***	***31***	***8***	***30***
C_{6b}b	3223	810	391	85	1023	39	18	189	65	5780
C_{6b}a	2912	735	351	88	909	41	17	180	61	5234
Re %	***10***	***9***	***10***	***-***	***11***	***-***	***5***	***5***	***7***	***9***
P_{6b}Di	661	168	86	26	211	5	14	36	17	1207
RT%	**49**	**48**	**43**	**61**	**39**	**70**	**5**	**47**	**30**	**48**

Ø *Monomeric Sugar Contents, Retention and Removal*

Sample	Man	Glc	Gal	Ara	Xyl	Rha	Glc A	Gal A	Fru	Total
F_{6a}	118	46	108	284	319	21	0	0	31	928
P_{6a}	113	42	104	274	310	21	0	0	32	896
R%	***5***	***8***	***4***	***3***	***3***	***2***			***-6***	***3***
C_{6a}b	113	45	102	265	303	20	0	0	30	878
C_{6a}a	12	2	10	24	32	0	0	0	0	53
Re %	***90***	***94***	***90***	***91***	***90***	***100***			***100***	***94***
P_{6a}Di	27	11	27	64	74	5	0	0	2	210
P_{6b}	102	38	92	259	289	20	0	0	28	829
R%	***10***	***10***	***11***	***6***	***7***	***4***			***13***	***8***
C_{6b}b	126	49	116	300	344	23	0	0	38	996
C_{6b}a	78	30	72	174	201	13	0	0	22	591
Re %	***38***	***38***	***38***	***42***	***41***	***44***			***42***	***41***
P_{6b}Di	44	17	39	106	123	8	0	0	12	349
RT%	***14***	***17***	***15***	***9***	***9***	***7***			***8***	***11***

Ø *Hemicelluloses Percentage (Hemicelluloses/Total Sugar)*

Sample	Man	Glc	Gal	Ara	Xyl	Rha	GlcA	GalA	4-O-Me-GlcA	Total
F_{6a}	97	95	80	25	75	66	100	100	100	88
P_{6a}	96	94	76	19	72	60	100	100	100	85
C_{6a}b	98	97	86	29	78	76	100	100	100	92
C_{6a}a	99	100	96	72	88	100	100	100		98
P_{6a}Di	98	96	81	36	77	63	100	100	100	90
P_{6b}	95	93	72	12	67	39	100	100	100	80
C_{6b}b	96	94	77	22	75	63	100	100	100	85
C_{6b}a	97	96	83	34	82	76	100	100	100	89
P_{6b}Di	94	91	69	20	63	38	100	100	100	77