TAMPERE UNIVERSITY
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ULTRAFILTRATION OF LIGNIN SLURRY

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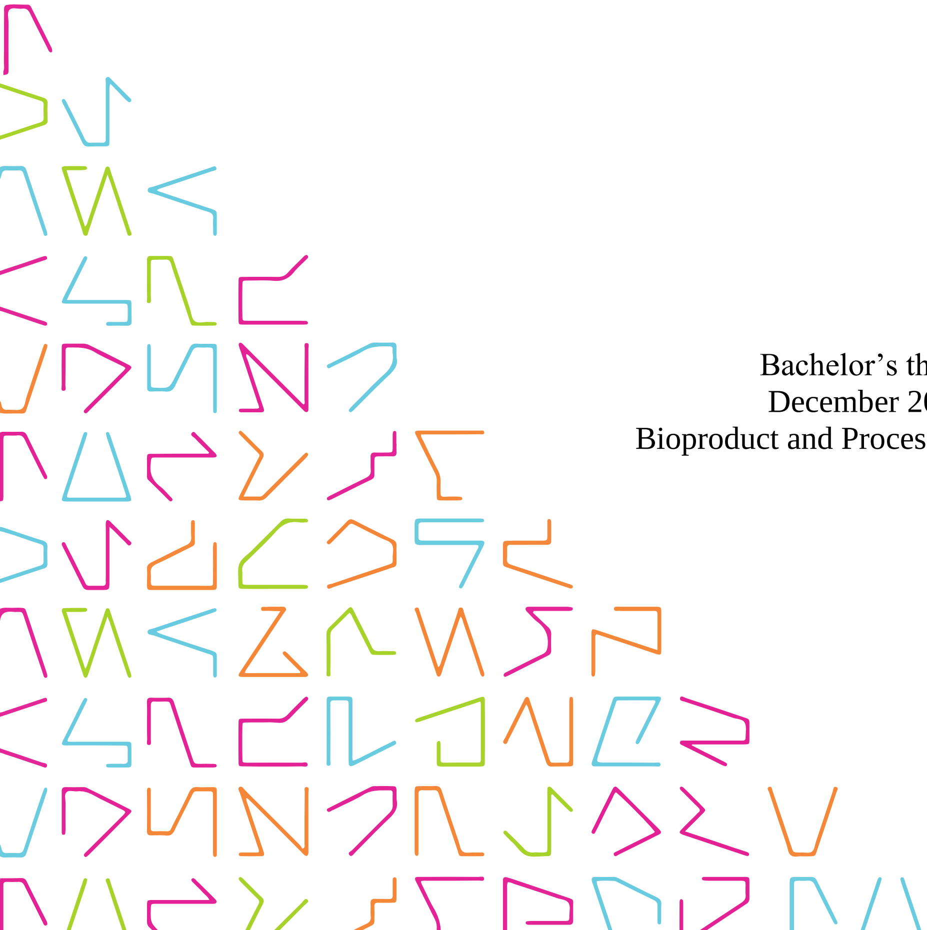

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ABSTRACT

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Ultrafiltration of Lignin Slurry

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This thesis consists of theory and experimental parts. The theory concentrates on the lignin, ultrafiltration and in its advantages and applications. The experimental part shows results for different membranes used in ultrafiltration through figures and comparisons. The laboratory results complete the overall results. The work was done for Valmet Technologies Oy and the tests were conducted in Valmet's R&D Center in Messukylä, Tampere.

The first purpose of this study was to gather information on different membranes and their possible advantages to ultrafiltration and hydrothermal carbonization (HTC) process. The aim was to decide whether ultrafiltration affects the lignin slurry and how the behavior of the membranes varies compared to each other. The second aim of this thesis was to increase the yield in lignin slurry by ultrafiltration technology provided by Valmet.

The trials were done with Valmet's Optifilter CR250/2 and various membranes. First, results were gathered from five different membrane combinations in recycling, concentration and dilution stages. Then, a concentration trial was conducted and finally, laboratory results were made. The results were then compared.

The results show that P and RC membranes compared to P10 and P20 membranes give similar laboratory results. The concentration trials show that there are differences between these membranes in permeate flux rates. P10 and P20 membranes are tighter compared to P and RC membranes and therefore the differences are explained. It takes more time to filtrate with P10 and P20 membranes, which can affect the expenses in the used processes. The yield in lignin slurry is higher in the concentrate, but in the permeate fluxes the dry solids are reduced.

In conclusion, both mentioned membrane combinations give similar results and there is no big difference to be seen. Ultrafiltration has many advantages and it is preferred to be used in HTC process as well. These results, however, need more studying to confirm what combination works the best. More stable conditions should also be created in order to achieve more reliable results. Temperature can be controlled, which would have an effect on the overall results. The particle sizes of the permeate fluxes after filtrating with different membranes would have been interesting to see. These can be predicted from the membranes pore size, but the shape of the particle cannot be seen. Altogether, the both aims of the study were fulfilled and the behaviors of the membranes are compared and discussed.

Key words: ultrafiltration, lignin, membrane, permeate flux

CONTENTS

1 INTRODUCTION

This thesis consists of literature and experimental parts. The literature part concentrates on lignin, ultrafiltration, different types of membranes and HTC process. In the experimental part, there are graphs on how ultrafiltration works with different membranes in different stages of the trial. Comparison and results are shown in this thesis. The aim of the thesis is to collect data from ultrafiltration with different membranes and compare the results. The suitability of the membranes for the HTC process is discussed. Valmet's aim was to gather information on the different membrane combinations and how they affect the lignin slurry.

Ultrafiltration of lignin slurry is a compact view on how ultrafiltration functions for lignin slurry and how it could be used in future. In the end of the thesis there is a discussion section where the work is evaluated and discussed in detail. The thesis was done for Valmet Technologies during the year 2017.

2 LIGNIN

Lignin is an aromatic hydrophobic polymer or a macromolecule and it is the second most abundant natural polymer in the world, surpassed only by cellulose. It is found from almost all vascular plant cell walls. It gives plants their rigid structure and it is the only polymer in cell walls that is not composed of carbohydrate monomers. It also reduces the transport of water through cell walls. Lignin has an aromatic functionality and is therefore unique and also the only large scale biomass source of its kind. (Lignoworks. 2016.: Wallmo H. 2008, 5.)

Lignin consists of phenyl propane units connected to each other in an irregular way either by ether or carbon-carbon bonds. Lignin's three different phenyl propane monomers are shown in the figure 1. Coniferyl alcohol occurs in all species and is the most dominant polymer in softwoods. Syringyl alcohol units are to be found from up to 40 % of hardwoods. For example, grasses can also consist of coumaryl alcohol units. (Lignoworks. 2016.: Wallmo H. 2008, 5.)

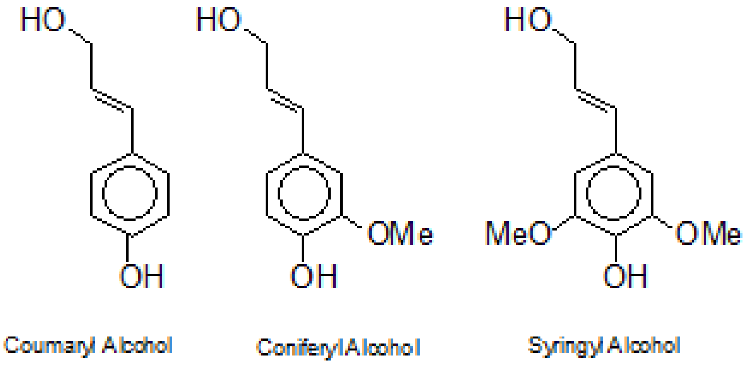


FIGURE 1. Lignin's three different phenyl propane monomers. (Lignoworks 2016, modified)

The proportions of the building units in lignin vary between different species. The overall structure of lignin can be described as a random, cross-linked, amorphous network consisting almost only of these phenyl propane units. Lignin protects cell wall polysaccharides from microbial degradation, it is one of the most important limiting factors when converting plant biomass to pulp or biofuels. Removal of lignin is a costly process and new methods to its removal are developed continuously. (Vanholme B. et al. 2010.: Wallmo H. 2008, 6.)

In general, lignins can be roughly classified into three groups: Softwood, hardwood and grass lignins. Besides these native lignins, which are typically separated from the wood in the form of "milled wood lignin" (MWL), "dioxane lignin", or "enzymically liberated lignin", there are several industrially based technical lignins that are by-products of the chemical pulping. Kraft lignin (or sulfate lignin), alkali lignin (or soda lignin), and lignosulfonates are derived from Kraft, soda-AQ, and sulfite pulping of wood. (Jingjing L. 2011, 8-9.)

As with many other branched biopolymers, lignin is considered to be polydisperse. Chemical treatments that degrade lignin will increase polydispersivity further. According to Wallmo, hemicelluloses can interact and bond with lignin molecules via so called “lignin carbohydrate complexes” (LCC). (Wallmo H. 2008, 7.)

The total amount of lignin varies considerably between different species. For example, softwoods contain a rather high amount of lignin, approximately 27 % and hardwood approximately 20 %. The largest fraction of lignin in wood is found from the stem of the tree. Wallmo writes that at least 70 % of the lignin in softwood (spruce) is found in the secondary wall of the fibers. Rest of the lignin is to be found between the fibers, in the middle lamella and cell corners. The same applies to hardwoods, with the exception that only 60 % of the lignin is found from the fibers. (Wallmo H. 2008, 7.)

According to Calvo-Flores et al. there is no single definition on what is lignin due to its complexity and its diverse structural composition. Lignin is not constitutionally defined compound. It is rather a physically and chemically heterogeneous material. All of lignin’s phenolic compounds or monolignols, conjugate variously in the biosynthesis process to of lignin to form a 3D polymer, which does not have an ordered and regular macromolecular structure. These processes of formation of phenylpropanoid macromolecules, or as said, lignin, is called lignification, which includes the biosynthesis of monolignols, their transport to the cell wall, and the polymerization into the final macromolecule. (Calvo-Flores et al. 2015, 12.)

2.1 Industrial applications of lignin

Removing lignin from black liquor is one effective way of recovering valuable organic substances for alternative use. Lignin has a high heating value (26,7 MJ/kg). This heating value is the highest value among all natural carbon polymeric compounds. Therefore, lignin is used in heat and power generation and in combustion units of a paper factory for example. The total amount of lignin that can be withdrawn is specific to the mill at hand and it depends on the heating value of the black liquor and the recovery boiler option. The main type of lignin produces in today's commercial processes is lignosulphonate, which is produced from the spent liquor in the suplhite process. The annual production of lignosulphonate is approximately 1 million tonnes per year worldwide. One advantage of kraft lignin is that the molecular weight distribution is smaller and in many applications, sulphonated kraft lignins are preferred. The worldwide potential of producing kraft lignin is enormous compared to the present market. (Wallmo H. 2008, 8-9.; Calvo-Flores et al. 2015, 252.)

According to Paterson, the 300-million-dollar lignin business today is dominated by products from sulphite-pulping liquors, originally based on the need to solve a pollution problem and to replace nonrenewable sources. Today it is a chemical business associated to the pulp mill. The formed lignin products are mainly directed to the process industry, but increasingly higher value products are produced over time. The lignin business faces high R&D costs, and has thus select carefully which markets to serve. (Paterson R. J. 2012, 69.)

There are many examples of pelletizing and related techniques associated with lignin. It is said that one of the most significant examples of linin as a binder is based on lignosulphonates, which are effective and economical adhesives, acting as binding agents in many industrial goods. A common binding agent for this purpose is a system called LignoBond, which was invented in the late 80s. Lignin has also been used in the manufacturing of packaging materials. The addition of lignin creates a barrier on the sheet, producing a higher quality material than conventional recycled paper. Also, lignin has antibiotic and antioxidant activity, which makes it a good component in a mixture for livestock feed. (Calvo-Flores et al. 2015, 253-254.)

Advancements in science and technology relating to lignin applications relies on vital and adequate information about lignins themselves, which requires versatile and sophisticated analytical methods specifically for lignins. Traditional degradative methods for lignin analysis still play an important role in lignin-related research and new alternative methods continue to emerge providing new insights into lignin structure and the associated biosynthetic pathways. Lignin is a complex polymer and its structure may not be fully explained until this day. However, lignin's composition, functionality, purity, molecular weight and degree of cross-linking, which are highly dependent upon the origins of lignin and the methods used to prepare it, largely determine its physicochemical properties and define its potential applications. (Fachuang L. 2014, 7, 8.)

The ratio of syringyl/guaiacyl (S/G, form of phenylpropanoids) units is commonly used to describe lignin's composition and to predict its reactivity under various processing conditions. The molecular weight and molecular weight distribution of lignin are important characteristics that affect lignin's chemical and physical properties. (Fachuang L. 2014, 7-8.)

According to Borregaard LignoTech (which is a world leader in binding and dispersing agents based on lignin), lignin's industrial applications can be anything from agricultural applications to binders, industrial cleaners and ceramics. Lignin's broad possibilities interest researchers and companies. Lignin is a natural byproduct for example when making cellulosic ethanol, kraft pulp of sulfite pulp and thus it brings great opportunities along. According to Toledano, lignin is considered a wasteproduct and it usually is used for energy generation. This is very common in paper and pulp industries and it is said that they together produce 40-50 million tons per year of lignin and from that amount only 1,5 % is commercialized as lignosulphonates or so called kraft process derived lignin. (Borregaard LignoTech; Folkedahl B.; Toledano A. et al. 2009, 1.)

Fachuang claims that kraft lignin accounts for about 89% of the production of chemical pulps, is obtained by pulping in an alkaline medium and is insoluble in water. The sulfite process produces sulfonated lignins, which are soluble in water containing suitable counter ion (Na+, Ca2+, Mg2+) due to the presence of a sulfonic acid linked to the backbone of lignin. Currently, a new class of sulfur-free lignins can be obtained by solvent pulping processes and soda pulping of agricultural crop residues. Sulfur-free lignins are water insoluble at neutral or acidic pH, but soluble in alkaline solutions or organic solvents. For example, lignin is used to replace harmful pesticides and CFR's. Lignin, besides being an anti-oxidant compound and good sorbent for pesticides, also absorbs UV light. This feature is the basis for the enhancement of biological pest control used as an alternative to chemical control, which is a better option for the environment. (Fachuang L. 2014, 15.)

Lignin can be extracted in large quantities, which makes it a good candidate as raw material especially when petrochemicals become more and more expensive. The interest for lignin as a feedstock is growing. According to Valmet, in the future lignin could become the main ingredient in production of liquid fuels, plastics, fiber composites, binders, technical carbons and much more. (Valmet. 2017, 3.)

2.1.1 Utilization of lignin in carbon fibers and plastics

Fachuang says that carbon fibers have been used as reinforcing materials since the 1950s and they are synthesized by a carbonization process, where a precursor fiber is thermally treated. They have high stiffness and tensile strength and therefore they are suitable for example for automotive industries, sports equipment and construction. However, carbon fibers are expensive material and they are thus replaced by lignin, which is a low-cost renewable material. “Considering the abundance of lignin in nature and the increase in lignin production as a residue of the emergent cellulosic ethanol industry, lignin might be the key to overcome the cost-limiting factors of carbon fibers.” (Fachuang L. 2014, 16.)

Although plastics have desirable properties, such as low cost and durability, they are not easily degraded. This is due to their barrier properties and high molecular weights. Furthermore, as plastics were recently created by man, there hasn’t been sufficient time to select for enzymes capable of degrading them. Consequently, the incorporation of lignin into plastics to increase their biodegradability has shown good results, says Fachuang. Studies have shown that benzylated lignin had similar properties to common plastics and wood-plastic composites. Lignin is replacing more and more plastics, which is good for lignin- based industries and environment as well. (Fachuang L. 2014, 16-17.)

However, byproduct lignin can be processed for example throughout gasification and catalysis and can therefore be used in various applications. Therefore, lignin must be considered as a product with many potentially attractive applications from an economic and also ecological point of view. First, lignin types and each species present in the processes have to be known. (Borregaard LignoTech; Folkedahl B.; Toledano A. et al. 2009, 1.)

3 MEMBRANE FILTRATION

Purchas says that the most important properties of a fluid in industrial filtration are viscosity and density. Density is generally only significant when the separation depends on a difference in density between the fluid and the particles. Viscosity is more widespread when it comes to its effects. It is also easier to control, since it is more sensitive to temperature changes. Therefore, the rate of filtration of liquids can be greatly accelerated and modified. (Purchas D. 1967, 7.)

Membrane technology means separation technology, where particles are separated structurally through different membranes. Separating ingredients and permeability of the membrane can be based on particle size, electrical charge or solubility. Separation needs an opening force – something that sends the molecules on the move. Driving force can be pressure difference, concentration difference or electrical field. In membrane technologies the driving force is concentration difference. The most important difference between basic filtration and membrane filtration is that it is possible to separate also solute components with membranes. (Heinonen R. 2016, 8.; Cheremisinoff N. P. 1998, 169.)

Membrane technology is an emerging and growing technology and it will be increasingly important in people’s lives. Today, various membrane processes have found numerous industrial applications from dairy to water purification, sea and brackish water desalination, gas and vapor separation and air pollution control to name few. Membrane technology applications continue to widen stimulated by the developments in membrane technology area. Technology advancements are for example improved membrane materials and membranes with better chemical, thermal and mechanical properties or better permeability and selectivity characteristics, as well as by the decrease of capital and operation costs. (Wang et al. 2010, 2.)

In general, membrane filtration technologies are used to concentrate, clean or fractionate different chemical compounds and molecules in liquids. The advantage in membrane filtration technologies is that no external additives such as solvents are needed. Also, the processes work in moderate temperatures, when they do not affect biological compounds’ structures. They also have low energy consumption rate and the instrumentation is easily build. Altogether, membrane filtration technologies don't affect the nature as much. (Heinonen R. 2016, 8.)

“A membrane is a thin layer of semi-permeable material that separates substances when a driving force is applied across the membrane” (Membrane Filtration). A membrane is basically anything between two phases that is semipermeable medium, which transmits only molecules or ions of particular size or charge. Membrane processes are increasingly used for removal of bacteria, microorganisms, and natural organic material. They can impart color, tastes and odors to water and react with disinfectants to form disinfection byproducts. (Membrane Filtration; Smolander S. 2015, 25.)

According to Simon, the membrane industry did not exist until the early twentieth century. The main research on membrane separation phenomena was aimed at elucidating the physicochemical principles of the process, and the mechanism of diffusion. However, some of these early-stage achievements still impact on the academic research and industrial applications today. When using traditional filtration methods, such as paper or metal net, fluid or gas flows are separated from unsolved solid particles. Membrane filtration widens filtration possibilities so that it is possible to separate colloidal, molecule or even ion sized impurities from water and gas flow. Membrane filtration can be used, when concentrating particular substance by removing solvent or when separating two components from each other in a fluid flow or when removing impurities for example in waste water treatment. (Smolander S. 2015, 25.; Simon J. 2010, 2.)

Fundamentals of membrane and membrane processes is presented in the figure 2.

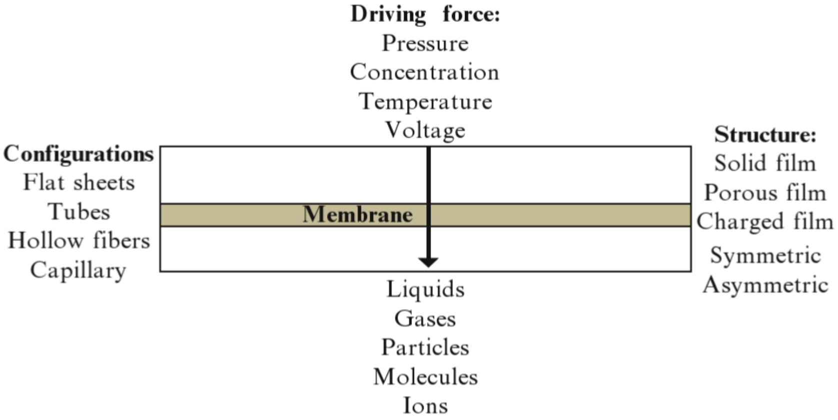
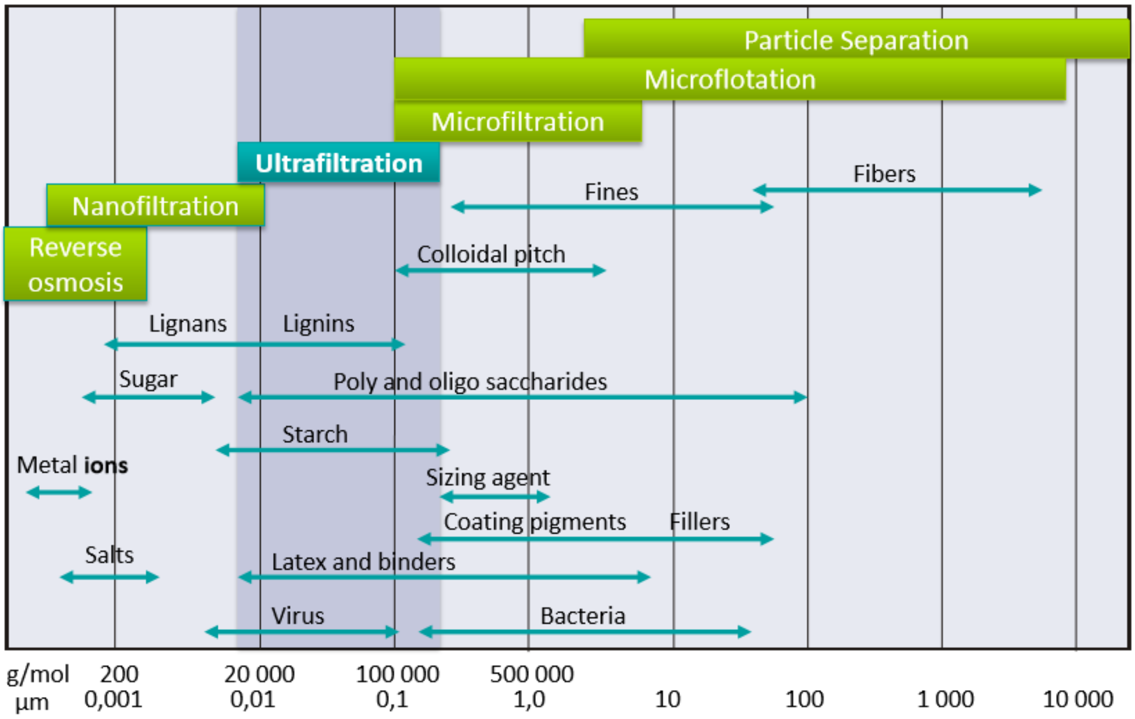


FIGURE 2. Fundamentals of membrane and membrane processes (Wang et al. 2010, 3.)

Membrane technology also allows the separation from the black liquor of different lignin fractions with a specific molecular weight being able to be used in the synthesis of several high value-added products for example chemical reactants, resins and biocomposites and antioxidant agents. (Toledano A., et al. 2010. 38-43.)



PICTURE 1. Membrane separation (Metso, OptiCycle R Process)

In the picture 1 a membrane separation process for Valmet’s OptiCycle R process is presented. Ultrafiltration process is marked with blue colour in the picture. Ultrafiltration is effective for lignins, poly and oligo saccharides, starch, latex and binders and viruses. The picture also shows the range where ultrafiltration works the best. Other filtration methods are presented on the picture with green colour. (Metso, OptiCycle R Process.)

According to Valmet “membrane filtration is based on continuous cross flow filtration, which is the main key for successful membrane filtration”. For example, this technology prevents particles from penetrating membrane pores. With cross rotation (CR) technology, cross flow is enhanced with cross rotation. Optifilter CR uses this technology, which is patented by Valmet. Valmet’s OptiCycle W is based on this same technology: It uses high velocity (>10 m/s), high turbulence and low pressure difference in order to give the best end result to a customer. (Metso Paper, OptiCycle W.)

Microfiltration and ultrafiltration have initially gained rapid acceptance as processes that provide a high level of particle, turbidity and microorganism removal. They are now being employed in conjunction with various unit processes to provide removal of both organic and inorganic materials. In the drinking water field, MF and UF have grown phenomenally during the past 20 years as filtration technologies in the use of low-pressure hollow fiber technologies. “In wastewater reclamation, MF and UF have enjoyed a similar level of growth, where the processes have essentially replaced media filtration as the preferred method of pretreatment prior to reverse osmosis for advanced reclamation projects.” (Delphos P. J. 2016, 2.)

Figure 3 emphasizes the differences between reverse osmosis, nanofiltration, ultrafiltration and microfiltration. The figure shows the sizes of the molecules and particles that are separable with a particular technology. Membrane pore sizes and pressure in bars are also marked on the figure. Pressures are higher in the smaller particle sizes accepted technologies such as nanofiltration and reverse osmosis.

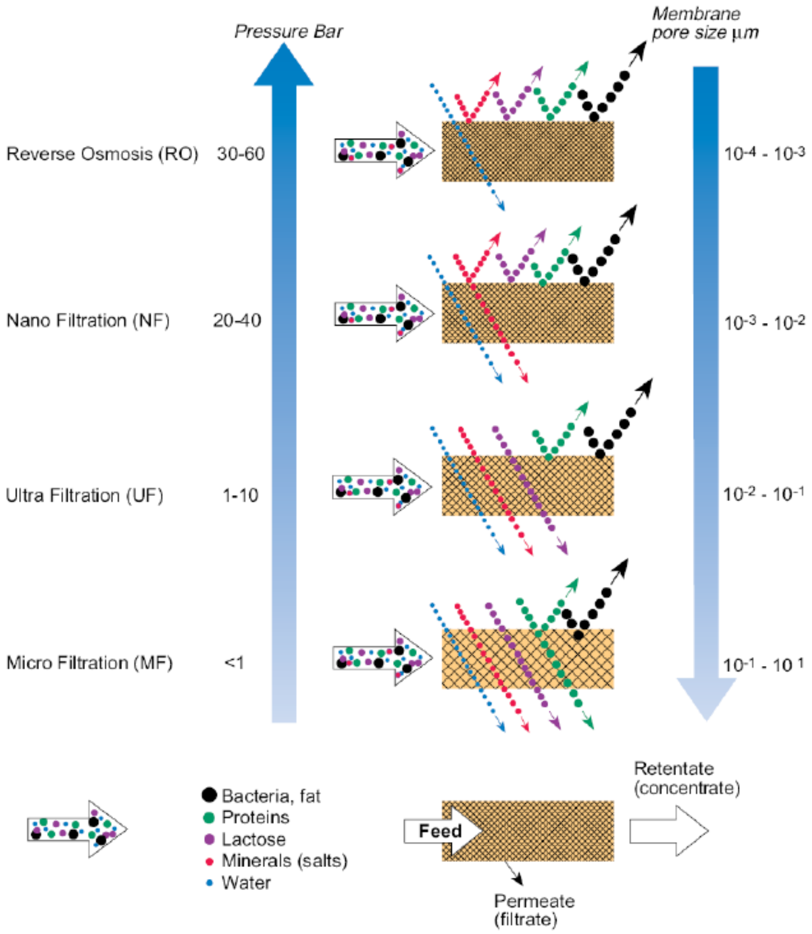


FIGURE 3. Membrane filtration methods and the compounds filtrated by their membranes (Heinonen R. 2016, 10.)

There has been a significant growth in used membrane technologies due to several important factors such as lower costs, public sensitivity and broader applicability. Also changes in regulatory system has affected the use of these technologies. (Delphos P. J. 2016, 4.)

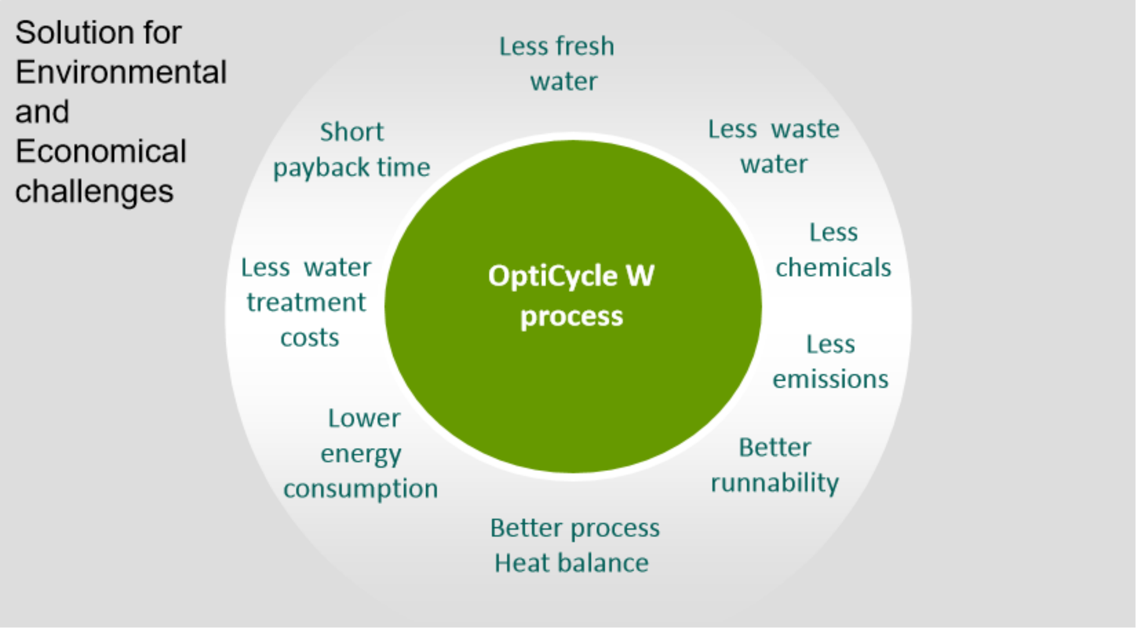
3.1 Ultrafiltration, UF

In general, ultrafiltration UF is a process of separating extremely small particles and dissolved molecules from fluids and it is used in wastewater treatment and in all kinds of separating purposes. Valmet uses ultrafiltration and Optifilter (shown in paragraph 6) to purify water in (chemi)mechanical and chemical pulping processes for example to remove and separate colloidal resins. Removal of resins has several benefits. To mention few, it lowers bleaching chemical consumption, gives better paper quality and lowers energy consumption at effluent treatment. (Metso, OptiCycle R Process.)

Ultrafiltration is a membrane filtration process based on a pressure gradient, which is used to purify, concentrate or separate large molecular compounds and colloidal particles from the feed. For example, UF is an optimal preliminary filtration method in RO's sea salt removing phases. (Smolander S. 2015.)

Today, ultrafiltration UF is widely recognised in various industries, among which pulp and paper industry offers a potent area of application for ultrafiltration. "In a conventional process, the large amount of black liquor generated in pulp and paper industry is either discarded or treated in a destructive way to recover the inorganic chemicals at the cost of valuable organics." (Bhattacharjee C. 2006, 1.) UF of black liquor has been suggested to recover the valuable organics, to meet a part of the water requirements and to treat wastewater problems. Bhattarcharjee claims that one of the major drawbacks in the use of UF for treating black liquor is the decline of flux with time. "This may be attributed to gel formation, osmotic pressure retardation or fouling of the membrane resulting from reversible or irreversible pore plugging". Different pretreatment methods are available to tackle this problem. (Bhattarcharjee C. 2006, 1.)

In the picture 2 is presented OptiCycle W process and its advantages and challenges.
OptiCycle R and W are parts of Optifilter membrane filtration technology as well as white water treatment and recycling.



PICTURE 2. Metso OptiCycle W process (Metso OptiCycle W)

Metso OptiCycle W improves effectively water processes and their quality and therefore is sold to customers all over the world (Metso OptiCycle W process).

There are generally three methods of fractionation of lignin and membrane technology is one of them. It allows obtaining lignin fractions with defined molecular weight distributions by free-reagents treatment of black liquor. Membrane technologies interest researchers due to its implementation in fields such as food, chemical, biological and pharmaceutical industries. This technology operates in a simple and effective separation, concentration and purification of smaller and medium size processes. As written before, there are problems associated with fouling and cleaning cycle or in-service life of the membrane. The effectiveness of membrane technology depends on the type of membrane used and the particle size that it can retain. The great interest of membrane technologies lies behind UF-NF technology applications for energy recovery in the kraft process. (Toledano A. et al. 2009, 2.)

It is anticipated that in the future the use of membrane technologies will continue to grow as new products and treatment concepts are developed. It is also observed that the trend to larger capacity systems will continue.

3.2 Reverse osmosis, RO

Reverse osmosis is a reverse version of osmosis. Pressure brought from the outside (2 MPa – 10 MPa) is introduced to the concentrated solution's side in order to cross the osmotic pressure. Transportation of a substance stops, when the osmotic pressure and the hydrostatic pressure of the fluid levels are the same. Process is forced to move backwards and it is called reverse osmosis. Large molecular substances are left on the extremely dense pressure side of the membrane. These are removed as reject and through the selective membrane only small molecular substances such as water are passed by. Through the reverse osmosis, organic and inorganic materials such as dissolved salts, water and ethanol can be removed from various water solutions. For example, reverse osmosis is the most used method to separating salt from sea water. (Mäkelä M. 2006, 12.)

3.3 Microfiltration, MF

Microfiltration is used to separate bigger than 0,1 mm particles from liquids. The microfilters used in this method are so small that they can hold micro sized particles' microorganisms. These filters are disposable. By microfiltration it is possible to remove harmful bacteria from liquids. Microfiltration is therefore used in biological waste water treatment. Usually microfiltration units are placed on the treatment line before ultrafiltration and reverse osmosis units. Pretreatment is a vital part, since blocking of the membranes disturbs the separation process. Microfiltration can also be used as a part of other membrane filtration methods. Keys to effective microfiltration are membrane's uniform and even pore size, pore density and the thickness of the active layer. (Mäkelä M. 2006, 13.)

3.4 Nanofiltration, NF

Today nanofiltration is mainly used to cleaning drinking water and to soften water. It is used to separate substances one nano meter by size. In industrial applications nanofiltration is applicable to removing for example colourants. Nanofiltration works with a help of pressure and its usage is based on molecule size. In this method too, membrane technology is used and the technology is mainly used to remove salty compounds from organic substance, but it can be used in different applications. (Mäkelä M. 2006, 13-14.)

4 MEMBRANE MATERIALS

Different membrane materials' important properties are in general: High porosity, high polymer strength, good polymer flexibility, permanent hydrophilic character, good chlorine tolerance, wide range of pH stability and low cost. Preferred UF/MF membrane filtration are high in mechanical strength and durability. Examples of these materials are polyvinylidiene fluoride (PVDF), polysulfone (PS), Polyether sulfone (PES) and polyacrilonitrile (PAN). Polyethylene (PE) comes with low polymer cost. Membranes provide absolute barrier to particles greater than their pore size. A membrane process requires two bulk phases physically separated by a third phase, the membrane itself. (Wilf M. 2008.; Munir A. 2006.)

A simplified schematic representation of the different phases in membrane separation is shown in the figure 4. On the left side there is feed and on the right side there is a permeate. Arrows show the direction of the flow.

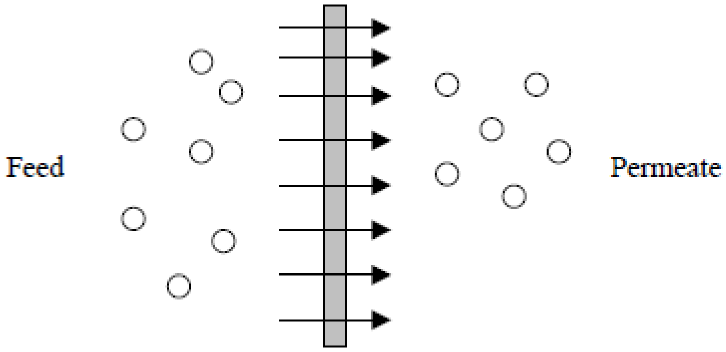


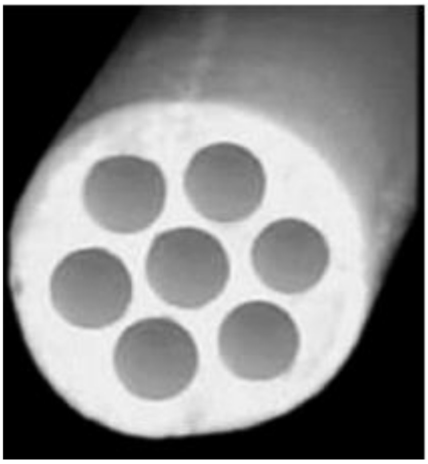
FIGURE 4. Schematic representation of the different phases in membrane separation (Munir A. 2006.)

The method presented in the figure 3 is used in MF, UF, NF and RO (reverse osmosis) depending on the size of the filter. The membranes used in MF and UF are clearly porous, when in NF and RO the pores are so small that the membranes used in these technologies are called homogenous and void-free membranes. In MF and UF the filtration happens mainly based on the pore size based segregation. The separation ability is also affected by the membrane surface's and the separated component's electrostatic interaction. (Smolander S. 2015, 25-26.)

The most common membrane materials are either organic polymers such as polypropylene (PP) or polyvinylidene difluoride (PVDF) or ceramic materials. Each has advantages and disadvantages for operation and maintenance and none should be completely disregarded in the search for the right membrane for an UF or MF application. (Delphos P. 2016, 54.)

The membranes used in membrane filtration can be divided into groups by their structure: Hollow fiber and spiral membranes, planar, tubular and spinning planar membranes. According to their structure, membranes can be also divided into three different groups: Asymmetrical, homogenous and composite. Homogenous membranes have homogenous structure along their whole thickness. Asymmetrical membranes consist of two layers: Thin selectively permeable layer and thick layer with larger pores, which provides mechanical strength properties and does not influence the water flow. It has also fabric support for reinforcing the thick layer. Most commonly used membrane in water treatment is hollow fiber membrane. Hollow membranes are 1 – 5 mm by diameter and inside they are hollow membranes. (Kainua & Hentilä. 2011, 18.; Akhmetova A. 2014, 18-19.)

In the picture 4 there is a close-up structure of a hollow fiber membrane. From the picture the structure is clearly visible. Tubular membranes are also hollow from inside. However, they are bigger in diameter compared to the hollow fiber membranes. (Kainua & Hentilä. 2011, 17-18.)



PICTURE 4. The structure of a hollow fiber membrane (Kainua & Hentilä. 2011, 18.)

4.1 Membranes used in UF

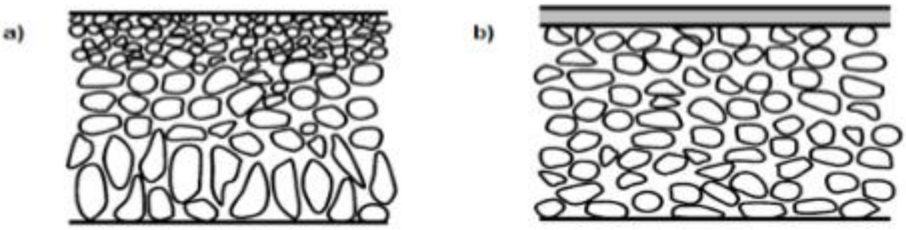
The membrane pore sizes used in UF vary typically between 0,01 - 0,1 µm. Instead of the particle size, UF-membranes separation ability is usually defined by unstandardized molecular weight cut-off (MWCO). MWCO describes how well the UF membrane can hold particular molar mass molecules. The MWCO value is the smallest molar mass of a molecule, that the membrane can hold up to 90-precent. In general, the MWCO values of UF vary from 1 to 500 kDa, which corresponds in particle size approximately 1 – 30 nm separation efficiency. (Smolander S. 2015, 31.)

The comparison between different UF membranes is difficult due to differences in membrane supplier's selection. Classification of UF membranes is hard due to the unstandardized MWCO values and it doesn't give a precise picture of their separation abilities. The suppliers define MWCO values under varying circumstances using different solvents with varying physical properties. Therefore, with the same MWCO values, the true pore size and filtration properties can differ a lot from each other. Even between membrane categories there are differences and some suppliers may name a membrane as a UF membrane instead of MF membrane. (Smolander S. 2015, 31.)

UF membranes are porous and asymmetric from their structure. They consist of a thin layer (0,1 - 0,5 µm) of fine porous surface layer, which is supported by thicker (50 – 150 µm) micro porous support layer. UF membrane's structure is called anisotropic, since its filtration properties are not the same in membranes thickness direction. Anisotropic structure enables great separation ability combined with a large flow, since the transmission degree is inversely proportional to its thickness. From an economic point of view, the surface layer should be as thin as possible. UF membrane's asymmetric structure can be manufactured in a one process or separately. (Smolander S. 2015, 32.)

Important factors in membranes used in ultrafiltration are pore geometry and the fluid flow. The pore size distribution and electrostatic interaction have an effect especially on the fluid flow as well. The surface charge on the pore wall causes an unequal partitioning of the charged ions into the pore. Therefore, the pressure-driven fluid flow causes a greater convective flux of the counter ions, that is, the negatively-charged Cl^- ions in a positively charged pore, through the membrane. (Oyama S.T & Stagg-Williams S.M. 2011, 333-341.)

Anisotropic's and TFC's (separately manufactured composite membrane) structures are presented in the picture 5.



PICTURE 5. A) Loub-Souriraja's anisotropic membrane and b) TFC membrane (Smolander S. 2015, 33.)

4.1.1 Ceramic membranes

UF membranes can be manufactured from organic and inorganic materials. Besides the polymeric membranes, also inorganic ceramic membranes are available. Ceramic membranes are often made of zirkoniumoxide (ZrO_2) and aluminiumoxide (Al_2O_3). Compared to polymeric membranes, ceramic membranes are superior in heat and chemical resistance. Despite the high price, their use can be economical in some processes, where good thermal resistance is needed or where regular washes with strong chemicals to prevent the blocking of the membrane are taking place. Ceramic membranes resist abrasion well, but they are quite fragile compared to polymeric membranes. (Smolander S. 2015, 36.)

Inorganic ceramic membranes are often used in demanding process conditions. Ceramic membranes can be used in the pH area of 0 – 14 and often in hundreds of degrees celcius. Process condition is limited by the module type, where the ceramic membranes are packed. One of ceramic membrane's advantages is its long usage age. Their usage age can be even 10 to 15 years. Their disadvantage is great investment and use expenses. (Smolander S. 2015, 40.)

4.1.2 Cellulose and its derivatives

Cellulose based membrane materials and specifically cellulose acetate are some of the oldest still used membrane materials. Cellulose's and its derivatives' structure is linear and their molecules are quite inelastic. These features are important in NF and RO applications. Cellulose polymer is very hydrophilic but thanks to its crystal structure and intermolecular hydrogen bonds it doesn't dissolve in water. Due to the hydrophilic features, cellulose derivatives work well in water based feeds cleaning. Cellulosetriacetate's (CTA) polymer structure consists of three acetate groups, which is why it is the most hydrophobic from cellulose based membrane materials. According to Smolander, cellulose polymer hydrolyzes in acidic conditions and deasetylizes in alkaline conditions. (Smolander S. 2015, 37.)

Cellulose based membranes usually have relatively low usage temperatures (30 – 40 °C). Cellulose acetate membrane's usage age varies depending on the process conditions, such as the quality of the water cleaned and the need for washing. In normal conditions, where there are not many washing times and the pH varies between 4 and 5,2, the operating life is approximately four years. The operating life decreases in higher pH values. The need for UF membrane washing depends on the quality of feed water, module type and the process quality and properties. (Smolander S. 2015, 38.)

4.1.3 Polymeric membranes

Polymeric membranes are formed of cellulose acetate or synthetic polymers, such as acrylates or polysulfones. Polymeric membranes are usually light in weight, thin, and require only little space. They are found in various configurations from hollow fiber to spiral wound to flat-sheet plate-and-frame membrane units. (Delphos P. 2016, 54.)

Cellulose acetate (CA) membranes, the most prominent membrane material in initial MF and UF membranes, are hydrophilic and thus are resistant to fouling by organic matter in the feedwater. They are able to withstand pH variations in the range of 5 to 8, though membrane lifetime is maximized by operation between 5.5 and 6 and temperatures as high as 50 °C. Cellulosic materials tolerate chlorine only in low concentrations, generally less than 1 mg/L. However, even these low concentrations will contribute to the oxidation of the membrane material over time. Generally, cellulose acetate membranes mostly have been replaced by other materials. Most synthetic water treatment membranes are hydrophobic. (Delphos P. 2016, 54.)

4.1.4 Polysulfone membranes

Polysulfone membranes are one of the most widely utilized materials in MF and UF membranes, especially in industrial applications, because of their relatively high tolerance to pH and resistance to oxidants. They can operate between a pH of roughly 2 to 13 and can withstand high temperatures of about 75 ℃. They are also quite resistant to oxidation by chlorine or other oxidants used in drinking water treatment. Polysulfones are replacing cellulose membranes in many places. Some suppliers promise that polyethersulfon membranes (PES) can take up to 125 ℃ of heat. PS and PES are stiff and strong due to their chemical structure. They also have a good creep resistance and dimension stability. Because of their good chemical and mechanical resistance, the membranes can be washed rather aggressively and thus compensate the contamination caused by the hydrophilic structure. PS and PES membranes have relatively low pressure tolerance. However, this is not a problem in ultrafiltration applications, since they are operated in low pressures. (Delphos P. 2016, 54.; Smolander S. 2015, 39.)

4.2 Membrane characteristics

Knowing certain characteristics of a membrane may allow easier selection of a membrane suitable for the desired application. For example, “knowledge of pore structure when inserted into an appropriate transport model will yield reasonable estimations of volumetric flux and rejection characteristics.” It is important to understand the potential properties of a membrane. Those are its morphological characteristics, such as surface porosity, pore size, pore shape, and roughness of the membrane surface. According to Delphos, membrane pores are not cylindrical holes cut perpendicularly through the membrane. Pores vary in shape and pores of many sizes can be present on a single membrane. (Delphos P. 2016, 55.)

In addition to the morphological characteristics, there are characteristics of a membrane that are measured through performance. Pure water flux for clean membranes is one of these performance-based characteristics. “It is the measurement of how permeable a membrane is using filtered deionized water normalized for the given conditions (temperature and pressure). A membrane displaying a high initial clean membrane flux could be a good candidate for operation at a low pressure, thus saving on energy costs.” (Delphos P. 2016, 55.)

One example of a different membrane is Multibore membrane, which has 7 single capillaries combined into one fiber. It also has PES blended with a strong, hydrophilic polymer and it is an asymmetric membrane formed from polymer blend. It has regular foam structure as active layer support. Multibore 7 structure is and single hollow fiber membranes are presented in the picture 6. (Wilf M. 2008, 36.)

PICTURE 6. Single hollow fiber membranes and Multibore 7-structure (Smolander S. 2015, 45.)

It is also anticipated that membrane materials will continue to become more robust with development advances. As the life cycle costs of ceramic membranes become more attractive, it is expected that companies offering this product will capture a reasonable market share and this will require a reduction in the capital costs of those systems. “A systematic approach to realize the value of robust membrane materials/systems, including their flexibility and durability in handling various types of changes in operating conditions, will also help to encourage the development of such products.” (Delphos P. 2016, 7-8.)

Technical advances are seen in the areas of membrane integrity testing, more effective cleaning regimes, and improved prevention of fouling. Membrane integrity designs are moving toward online testing with resolution that permits the estimation of for example virus removal. (Delphos P. 2016, 7.)

5 FACTORS AFFECTING ULTRAFILTRATION

Membrane filtration process’ effectiveness and functioning is strongly affected by membrane clogging. Clogging is considered as the biggest problem in membrane filtration. Clogging slows down the feed of the membrane filtration unit, when the drive parameters and conditions stay unchanged. Clogging leads to the rise of usage expenses, since the need for energy and washing increase and the usage age of the membrane decreases. Industrial membrane filtration processes are continuous processes, where the permeate feed and pressure are kept constant. (Smolander S. 2015, 55.)

Pre-treatment is typically applied to the feed water before entering the membrane system in order to avoid fouling. Pre-treatment is often used to remove foulants, optimize recovery and system productivity and to extend membrane life. It may also be used to prevent physical damage in membranes. Different types of pre-treatment can be used in conjunction with any given membrane type. Membranes can be fouled by organic or inorganic substances. Therefore, pre-treatment of the feed stream is required to control colloidal, organic, and biological fouling, as well as scaling. For low-pressure membranes, a number of pre-treatment methods are currently used. (Basile A. 2015, 90-91.)

Pre-treatment includes steps such as removal of large particles using coarse strainer, water disinfection with chlorine, clarification with or without flocculation, reduction of alkalinity by pH adjustment and using cartridge filters to remove final suspended particles. (Basile A. 2015, 91.)

5.1 Flux decline mechanisms

In porous membranes the permeate feed decreases instantly after the filtration of solution including impurities has started. The UF membrane fouling can be divided according to its causing factors: Particle or solution based or biological fouling. UF membrane clogging mechanisms can be roughly divided to filtrate cake layers, pores clogging due to particles and foulants adsorption on the surface of the membrane or pore walls. Flux decline mechanisms are called concentration polymerization and fouling. (Smolander S. 2015, 55.)

5.1.1 Concentration polymerization

The primary cause of fouling is concentration polymerization, which results in the deposition of the layer of material on the membrane surface. “Concentration polarization is the accumulation of rejected particles near the membrane surface causing the concentration near the surface to be greater than that of the bulk solution.” (Delphos P. J. 2016, 38.) When transmembrane pressure is imposed, particles are transported to the membrane and accumulate near the membrane surface. This creates a concentration gradient. As a result, particles diffuse back into the solution. The effects caused by concentration polymerization can be removed by lowering the feed pressure or concentration. Also a turbulence on the surface of the membrane reduce the forming of the layer. Countercurrent helps the cleaning of the formed cake and gel layers. (Delphos P. J. 2016, 38.; Smolander S. 2015, 56.)

The mechanism of concentration polymerization is described in the figure 5.

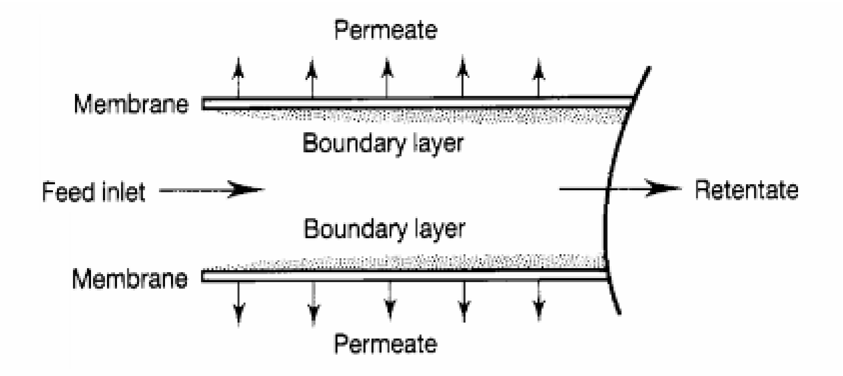


FIGURE 5. Development of the concentration polarization (or boundary layer) (Lewis M. J. 1996, 106.)

5.1.2 Fouling

Fouling in MF/UF membrane processes is often defined as “the gradual reduction in filtrate water flow rate at constant pressure (or similarly, an increase in trans-membrane pressure at constant flux), caused by adsorption or deposition of suspended matter within membrane pores or on the membrane surface.” (Delphos P. J. 2016, 39.) The fouling mechanisms are categorized as pore adsorption, pore blocking, and cake formation. Based on blocking filtration theory, permeate flux decline can be predicted for these three mechanisms. Pore adsorption and blocking are internal membrane fouling mechanisms, whereas cake formation takes place on the surface of the membrane and is defined as external fouling. (Delphos P. J. 2016, 39.)

Membrane fouling in crossflow MF and UF is a key factor affecting the economic and technological viability of the processes, which essentially depends on the permeate fluxes obtained and their stability with time. Therefore, the identification and quantification of the prevalent fouling mechanism and efforts to minimize its effects during a continuous filtration process are extremely important. (Cassano A. & Basile A. 2013, 164.)

The fouling behaviour depends on physical and chemical parameters such as temperature, pH, concentration, ionic strength and specific interactions. It varies depending on the type of the foulant agent. The degree of the membrane fouling determines the frequency of cleaning, the lifetime of a membrane and the membrane area needed. Thus, it has a significant effect on the cost, design and operation of membrane plants. Rejection and yields may also be affected by fouling. (Cassano A. & Basile A. 2013, 164.)

The membrane types and materials affect fouling substantially. Membrane material, pore size and the surface hydrophilicity affect fouling. Hydrophobic membranes adsorb proteins, whereas hydrophilic membranes attract more minerals such as calcium. Hereby, hydrophilic membranes are not as sensitive to fouling as hydrophobic membranes. The membranes used in ultrafiltration are always hydrophilic in order to prevent protein adsorbing. (Heinonen R. 2016, 19.)

Also, the process conditions affect fouling. Cross-flow-filtration is better than dead-end-filtration, where the substances held by the membrane form easily a cake on the membrane surface. Pressure difference, temperature and adjusting the turbulencity can reduce the fouling of a membrane. High pressure can remove formed cake from the surface and prevent reforming of a cake. Backflushing or backpulsing (changing the feed flow direction) removes the particles accumulated on the membrane surface. (Heinonen R. 2016, 20.)

Fouling mechanism for an ultrafiltration membrane is shown in the figure 6. Surface fouling is generally reversible; it is the deposition of solid material on the membrane that consolidates over time. Internal fouling is caused by penetration of solid material into the membrane, which results in plugging of the pores. Internal membrane fouling is generally irreversible. (Baker R. W. 2012, 258.)

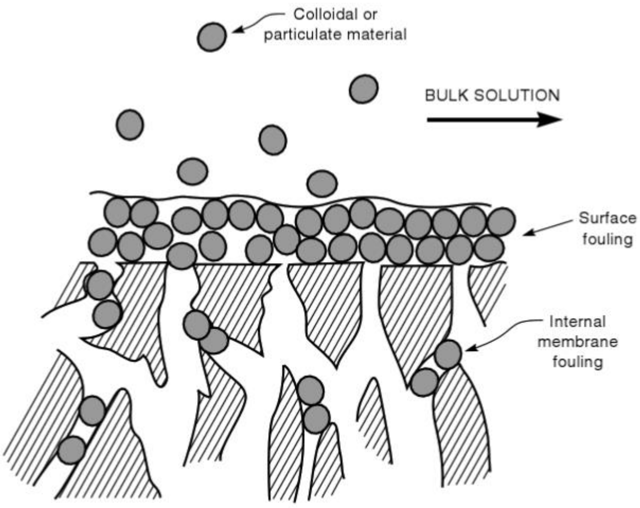


FIGURE 6. Schematic representation of fouling on an ultrafiltration membrane (Baker R.W. 2012, 258.)

The pore adsorption model assumes that permeate flux decline is attributed to the decrease in membrane pore diameter that results from particle deposition within membrane pores. On the other hand, the pore blockage model describes the decrease in permeate flux as the reduction of the overall number of pores caused by complete pore blockage by particles. The cause of pore volume reduction differs for each model, but both processes cause a reduction in membrane permeability. “The cake formation model, in contrast to the previous two, describes permeate flux decline (or increase in transmembrane pressure) by the formation of a particle cake layer on the membrane surface.” (Delphos P. J. 2016, 39.)

Formation of a cake occurs when a suspension contains particles that are simply too large to enter the pores. The increase in the mass of particle foulants deposited on the surface is proportional to the filtrate volume. Cake formation provides additional resistance to filtration that increases with operation time and causes transmembrane pressure to increase or the permeate flux to decline. (Delphos P. J. 2016, 39.)

Pore adsorption occurs when the diameter of the particle is smaller than the diameter of the pore. Particles are deposited on the pore walls along their entire length. This constriction of the pore changes the overall pore volume by decreasing the pore diameter while the overall number of pores remains constant. The change in pore volume is proportional to the filtrate volume. The hydraulic resistance is increased as a result of the deposition of particles within the pore. (Delphos P. J. 2016, 39.)

Also, when a suspension contains particles with diameters approximately equal to that of the membrane pores, pore blocking occurs. Pore volume is reduced by the blockage of individual pores. Therefore, the total number of pores is reduced, while there is no effect on pore diameter. Like pore adsorption, the change in pore volume is proportional to the filtrate volume. (Delphos P. J. 2016, 39.)

Delphos says that when a membrane is fouled, porosity decreases, hydraulic diameter decreases, and effective thickness increases. Fouling is a physical and chemical process between the membrane material and the solution that is filtrated. This causes the membrane's material characteristics to affect its fouling sensitivity. (Delphos P. J. 2016, 39.; Smolander S. 2015, 58.)

Methods of reducing fouling are different physical and chemical methods. These can be divided to pretreatment, design and operation methods. Pretreatment methods are for example prefiltration, flocculation, coagulation and carbon sorption. Design methods affecting and reducing fouling are element design, pulsetile, flow regime, moving surfaces and roughness. Operation methods are maintaining high cross-flow, periodic flushing and for example mechanical cleaning. Chemical methods are such as ion-exchange, dispersants, disinfectants and pH adjustment. (Cardew P.T. & Le M.S. 1998, section 7: 10)

5.2 Filtration conditions

Ultrafiltration processes depend highly on the process conditions at hand, such as process temperature and pH value. When operating in higher temperatures, the density and viscosity of a liquid decrease and water is able to penetrate the membrane easier and the permeate feed increases. The lower viscosity of the liquid also decreases the needed amount of pumping energy and therefore decreases the pumping expenses too. (Smolander S. 2015, 58.)

It is important to take the changes in the feed's temperature into closer consideration. For example, the decrease in temperature affects the feed flow decreasingly but this shouldn't be mixed up with the membrane clogging. Also, sudden changes in temperature can harm mechanically the membrane module. (Smolander S. 2015, 58.)

5.3 Cleaning of the membrane

Ultrafiltration unit's feed flow decreases over time due to resistance-phenomena. To regain the feed flow, membranes have to be cleaned up from time to time and the frequency of cleaning and the cleaning method depend on the quality of the feed, clogging mechanisms and the membrane and module type. It is important to optimize the cleaning cycle because of the membrane functioning and also because of the economical aspect. (Smolander S. 2015, 60.)

Too slight cleaning can result to useless membranes due to clogging, whereas too frequently happened cleaning can result to membrane polymer's premature wearing. Membrane's chemical cleaning can affect membrane's properties, such as membrane's morphology, hydrophilicity and charge. Cleaning the membrane also reduces the membrane modules operating time, since the module is not in use during the cleaning. Therefore, the time used in cleaning should be as short as possible. (Smolander S. 2015, 60-61.)

There are four methods used in membrane cleaning: Hydraulic, mechanical, chemical and electrical cleaning. The water used in cleaning should be the same quality as the permeate is. A common method for membrane filtration cleaning is countercurrent cleaning which is a hydraulic way of cleaning. In this method the permeate flow is turned to the counter direction in the end of the filtration cycle. Before and after countercurrent cleaning also forward current is used. (Smolander S. 2015, 61.)

6 VALMET’S OPTIFILTER CR250/2

Ultrafiltration technology used in this thesis is presented in this chapter. First, technical information with pictures is presented and then, operating value limits are presented.

6.1 Technical info

Valmet’s optifilter CR250/2’s general view is presented in the picture 7. CR comes from the words “cross rotation”.

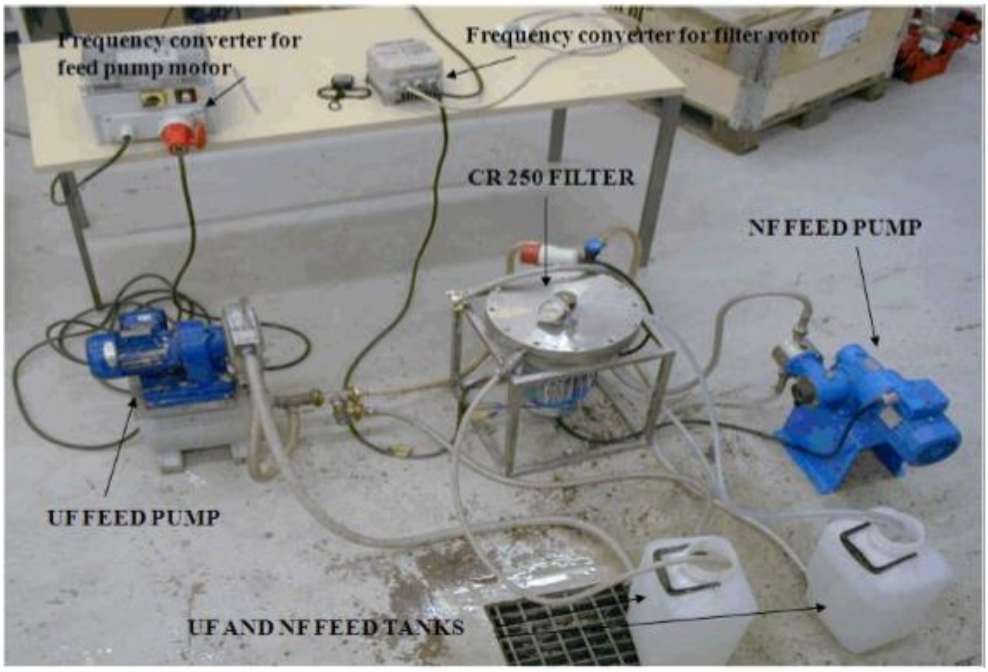
PICTURE 7. Valmet’s optifilter CR250/2 (Metso Paper/FPT)

Optifilter is portable and easily assembled. Its dimensions are given in the table 1.

TABLE 1. Main dimensions of Optifilter (Metso Paper/FPT)

Height, ca.	0,39 m
Width, ca.	0,365 m
Length, ca.	0,365 m
Volume, ca.	0,7 dm^3

Typical installation of the machine is shown on the picture 2



PICTURE 8. Typical installation of Optifilter CR250/2 (Metso Paper/FPT)

In the picture 8 an ultrafiltration (UF) pump, UF and feed tanks, CR 250 filter, nanofiltration (NF) feed pump, frequency convertor for filter rotor and frequency converter for pump motor are shown beside their operation units. Assembled version is shown in the picture 7.

6.2 Operating value limits

Optifilter’s operating value limits are presented in the table 2. It shows machine’s operating pressure ranges, minimum and maximum temperatures, pH-values and maximum particle size in feed for the filter. It is important to note that the allowed temperature, pH ranges and chemical limits for the membranes are defined case by case. (Metso Paper/FPT.)

TABLE 2. Operating value limits for optifilter CR 250/2 (Metso Paper/FPT)

Maximum allowed operating pressure	1000 kPa
Recommended differential pressure range	80 – 750 kPa
Minimum allowed differential pressure for rotor use	50 kPa
Lowest allowed operating temperature	20 °C
Highest allowed operating temperature	80 °C
Ambient temperature	10 – 40 °C
pH-range during filtration	3 - 11
pH-range during washing	1 - 13
pH-range during normal standby	6 - 8
Maximum particle size in feed	75 – 150 µm

Maximum allowed temperature change rate is 40 °C/h according to Metso Paper's information. Fast temperature changes should be avoided in order to avoid external leakages or other damages. Solids content and viscosity of feed and particularly concentrate are also limiting factors for the filter use. The acceptable particle size depends on the used solid material and more detailed evaluation is always case-specific. (Metso Paper/FPT.)

More detailed technical specifications are to be found from the appendix 1.

7 ULTRAFILTRATION APPLICATIONS

Ultrafiltration has various applications ranging from the processing of macromolecules to wastewater treatment. Some of these applications are fractionation of macromolecules, for example proteins, concentration of macromolecules, removal of salts and other low molecular weight compounds from solutions of macromolecules, removal of cells and cell debris from fermentation broth, virus removal from therapeutic products, harvesting of biomass, membrane reactors and effluent treatment. (Ghosh R. 2003, 13.)

According to Ghosh, food and biotechnological applications cover nearly 40 percent of current total usage of ultrafiltration membranes. Processing of biological macromolecules such as proteins and nucleic acids are assumed to be significantly important in the bioprocess industry. It makes good economic sense to develop cost-effective and scalable purification processes such as UF. When it comes to processing proteins, UF is mainly used for protein concentration, desalting, clarification and protein fractionation. (Ghosh R. 2003, 13.)

Membrane processes have many applications in the treatment of contaminated waste streams. The most common applications involve the removal and concentration of organic and inorganic contaminants from liquid waste streams. The waste streams can originate from industrial processes, contaminated groundwater, contaminated surface water bodies, or as by-products of other treatment processes. Membrane and filtration processes have historically been utilized for the treatment and purification of drinking water and nowadays membrane filtration’s applications are wide. (Cheremisinoff N.P. 1998, 171.)

Membrane technologies are also capable to integration with other technologies and it makes the application spectrum wider. Ease of integration is facilitated by the modular and scalable properties of membrane systems. These systems can be readily integrated with other remedial process equipment to enhance the effectiveness and economy of these systems. (Cheremisinoff N.P. 1998, 172.)

The industrial applications of ultrafiltration membranes are presented in the table 3.

TABLE 3. Industrial applications of UF membranes (Wang et al. 2010, 13.)

Industries	Applications
Automobile and household appliances industry	Recovery of electrophoretic paints from rinse waters
Metal-processing industry	Recycling emulsions used in metal forming
Food processing	Dairy: - Recovery of proteins from whey - Dietary milk production Recovery of Proteins from meat processing effluents Concentration of egg white Sterilization and clarification of beverages, especially wine Recovery of valuable constituents from starch and yeast processing effluents
Pulp and paper industry	Waste paper mill effluent treatment
Pharmaceutical industry	Sterile filtration of water or solutions Isolation, concentration and purification of biologically active substances (enzymes, viruses, nucleic acids, specific proteins) Fractionation of blood
Semiconductor industry	Production of ultrapure water
Water industry	Pretreatment before NF and RO

7.1 Food and biotechnology industries

For many heat unstable macromolecules, for example proteins and starches, concentration by UF at ambient temperature will minimize the heat-induced reactions which may adversely influence their functional behavior in foods. Some important functional properties are solubility, foaming capacity, gelation, emulsification capacity, fat and water binding properties. As explained before, ultrafiltration offers the opportunity to concentrate large molecular weight components without the application of heat or a change of phase. These components are rejected by the membrane, whereas the permeate produced will contain the low molecular weight components present in the food, at a concentration similar to that in the feed. (Lewis M. J. 1996, 97.)

UF is also very useful for recovering valuable components from food processing waste streams and fermentation broths. Lewis M. J. claims that “probably the greatest impetus has come from the dairy industry and dairying applications. However, in all applications, flux decline due to concentration polarization and fouling are probably the two most important practical aspects.” (Lewis M. J. 1996, 97.)

For example, milk is an ideal fluid for membrane separation processes since it contains about 30 - 35 % protein and approximately the same amount of fat (on a dry weight basis). Therefore, it is an ideal fluid for membrane separation processes. Perhaps the most important trend in the 80s was the move to a more health-conscious diet, and in this sense skim milk is more widely used as the starting material for yoghurts, low-fat cheeses and other desserts. Ultrafiltered milk also forms the starting material for some of these types of products. (Lewis M. J. 1996, 121.)

7.2 Other applications

In chemical engineering, environmental demands are rising the rate of membrane technology use. Also process substances circulation and cost savings caused by it are increasing membrane technology usage rate. In chemical engineering, as in many other fields, the most important uses are cleaning of gases and waste water. Using these methods is held in high regard due to their decrease in environmental emissions and pollutants. Valuable substances can be collected and reused in other processes. In chemical engineering, multiple separations happen in gas phase and thereby gas separation equipment are in common use in chemical engineering and technologies. One important application area is medicine industries. (Mäkelä M. 2006, 32.)

In wood processing industries, membrane separation is concentrated on pulp- and paper industries and their waste water cleaning and other cleaning systems. For example, paper machine’s closed water cycle is cleaned with reverse osmosis or ultrafiltration equipment from accumulated chemicals. Also, from the whitening water all the colourants can be removed by ultrafiltration. (Mäkelä M. 2006, 32.)

In metal industries membrane separation is used mainly to separate cut- and cooling liquids. These liquids are mainly oil emulsions and classified as environment debris. Also, collecting and reusing heavy metals and paint pigments are cost saving factors, which can be done by membrane separation methods. (Mäkelä M. 2006, 32-33.)

In textile industries membrane technologies and ultrafiltration is used to colourant and waste water and wash water treatment. There are new methods continuously developed and pilot-tested. (Mäkelä M. 2006, 34.)

7.3 Advantages of ultrafiltration

Ultrafiltration has a few advantages over competing separation techniques such as chromatography, electrophoresis and affinity separation. These are high throughput of product, relatively easy scale-up and the simplicity of cleaning and sanitation of equipment. Ultrafiltration is widely used for protein diafiltration, clarification and concentration but the potential for its use for protein fractionation is widely untapped. According to Ghosh, "a significant number of ultrafiltration users are unaware of its intricacies and, more importantly, the true potentials of ultrafiltration as a protein separation technique." (Ghosh R. 2003, 16.)

Ghosh says that it is still largely regarded as a simple sieving process where solute size is the criteria for separation. Early attempts to fractionating proteins purely based on size have been unsuccessful in the year of 2003. However, solute size is just one of the many factors that could be utilized for separation. Protein-protein interactions, protein-membrane interactions, the extent of concentration polarization and the predominant mode of protein transport are amongst several factors, which can be exploited for enhancement of protein fractionation. Most membrane researchers have confined their studies to the separation of simulated mixtures of proteins. "While this has undoubtedly led to a better understanding of the mechanisms of protein transport and separation, the lack of substantial application based research has kept ultrafiltration in the blind spot of potential users." (Ghosh R. 2003, 16.)

8 HTC AND LIGNOBOOST PROCESS

8.1 HTC process

The HTC process where the lignin slurry studied in this thesis comes from a company called SunCoal Industries from Berlin, Germany. The HTC means hydrothermal carbonization and the lignin slurry is a product of that process. Afterwards, this slurry is dried and the resulting lignin is collected and used in various applications.

According to Valmet, the pulp and paper industry produces large volumes of effluent treatment sludge. The sludge holds water, which makes it expensive to transport and dispose of. Furthermore, there are no energy-efficient methods of incinerating sludge, and the option of sending sludge to landfill will be limited in the future. Valmet’s and SunCoal’s HTC concept is a solution to these problems. (Valmet. 2017.)

HTC is an efficient biomass conversion technology using mild processing temperatures (180 – 250 °C) and water as the carbonization medium, under self-generated pressures. Several chemical reactions occur during the process including hydrolysis, dehydration, decarboxylation, polymerization, aromatization and condensation. As a consequence, carbonaceous solid fraction accompanied by liquid phase and minor gas phase are formed. In general, the solid carbonaceous material consists of particles with different shapes and size having functional groups on the surface and distinct properties such as a high energetic value, a high chemical and thermal stability, and a relatively high adsorption capacity. The HTC process has recently attracted researchers all over the world, though it was invented a hundred years ago by Bergius. HTC has been demonstrated to be an effective process for the production of functional carbonaceous materials from simple monosaccharides, such as glucose. (Wikberg H. et al. 2016, 237.)

The HTC process aims to reducing the management costs of the sludge. During the HTC process, the sludge is transformed into a solid biofuel. Sludge management costs are reduced while also cutting CO^2 emissions. The end result is a sludge press cake ready for incineration. It is a solid biofuel, which can replace the use of fossil fuels. In the HTC process, the structure of the sludge is transformed by removing chemically bound oxygen and hydrogen as well as intracellular water. “The total sludge mass at the start of the HTC process can be reduced by up to 70%, using only 25% of the energy compared to thermal drying.” The remaining sludge press cake is explosion-safe and has good handling and transportation characteristics. (Valmet. 2017.)

In addition to sludge management, HTC is also a solution for upgrading biomass to bio-based technical carbons. Biomass or sludge enters a reactor at high pressure and high temperature. Water is removed separately. The drained precursor is then activated to produce activated carbons. “One of the advantages of Valmet’s HTC concept is that the quantity of impurities as ash is reduced resulting in a higher yield and higher quality end products or precursor for technical carbons.” (Valmet. 2017, 3.)

The HTC pilot plant is located in Ludwigsfelde, Germany and it includes a research laboratory as well. In developing the HTC process and its technologies a couple of steps have been critical. The researchers did systematic research for refining various types of biomass (wood, leaves, grass and grass cuttings to mention few) through hydrothermal carbonization. Another important factor has been process optimization with high energy yield. Also, issues of energy efficiency, water handling and optimal input and output procedures have been under intensive research. (SunCoal)

In 2011 the pilot plant was converted for customer testing purposes, encompassing the following areas: Preparation of capacities for carbonization and optimization with customer biomass, specific analysis of biomass, biocoal and process water in the in-house lab and with external partners and production of product samples for further research and development projects, also with external partners. Today, the HTC pilot plant is running and producing lignin slurry and different coals for further studying and for customer use. A part of the HTC plant is presented in the picture 9. (SunCoal)

PICTURE 9. HTC pilot plant (Valmet. 2017.)

8.2 Increasing the yield by ultrafiltration

The aim of this thesis is to increase the yield in lignin slurry by ultrafiltration technology provided by Valmet. Today, the ultrafiltration step is missing from the HTC pilot plant and it is important to find out, what could be done with ultrafiltration and how much it would increase the yield. The findings in this thesis are presented in the results section.

8.3 LignoBoost process

Black liquor is a complex mixture of inorganic salts, water and organic material. Each of these materials play an important role when defining the characteristics of black liquor. Table 3 shows the typical chemical composition of kraft black liquor from North American wood species. The chemical charasteristics of the kraft black liquor affect properties such as viscosity, heating value, boiling point rise, heat capacity, density and thermal conductivity.

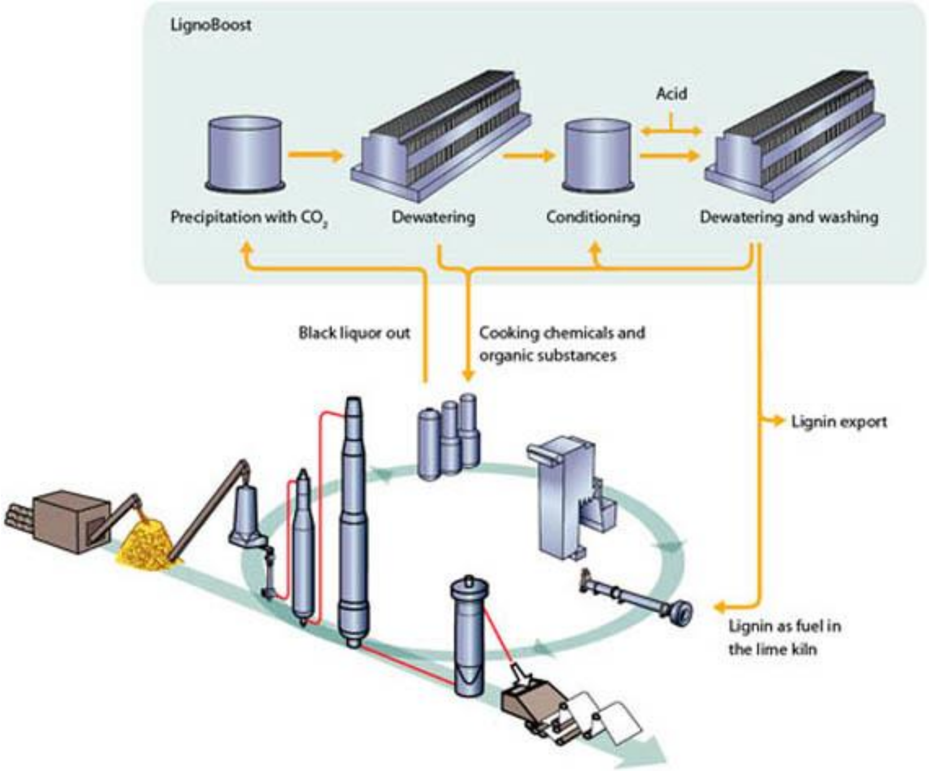
TABLE 4. Chemical species and elemental composition of kraft black liquor from North American wood species (Wallmo H. 2008, 4.)

Chemical species in kraft black liquor		Elemental composition of kraft black liquor	
Alkali lignin	30 – 45 %	Carbon	34 – 39 %
Hydroxy acids	25 – 35 %	Hydrogen	3 – 5 %
Extractives	3 – 5 %	Oxygen	33 – 38 %
Acetic acid	5 %	Sodium	17 – 25 %
Formic acid	3 %	Sulphur	3 – 7 %
Methanol	1 %	Potassium	0,1 – 2 %
Sulphur	3 – 5 %	Chloride	0,2 – 2 %
Sodium	15 – 20 %	Nitrogen	0,04 – 0,2 %
		Others	0,1 – 0,3 %

The composition of black liquor depends on the cooking conditions and the type of wood used. According to Wallmo, during the digestion the cooking chemicals do not only degrade the lignin in the wood chips: since the hydroxide ions are not selective toward lignin, some of the cellulose and hemicellulose are also degraded. A large part of the carbohydrate losses happens during the heating up period of the digestion stage. The most important hemicellulose reactions during kraft pulping re-peeling and alkaline hydrolysis, followed by secondary peeling. (Wallmo H. 2008, 4-5.)

The LignoBoost process produces lignin of high purity using a relatively small amount of wash water. The process consists of precipitation, filtration and washing steps. “The lignin is precipitated by acidification in the precipitation vessel and filtered in the following filtration step. Instead of washing the lignin directly in the first filtration stage, the filter cake is re-dispersed in water at low pH, preferably between pH 2 and 4.” (Wallmo H. 2008, 13.) The resulting slurry is filtered once again and washed by displacement washing with acidified wash water. Most of the changes that occur in the lignin particles take place in the re-suspension stage. (Wallmo H. 2008, 13.)

LignoBoost works in conjunction with evaporation. According to Valmet, Black liquor is taken from the evaporation plant and the pH is lowered with CO^2. The precipitated lignin is then dewatered using a filter press. “LignoBoost then overcomes conventional filtering and sodium separation problems by redissolving the lignin in spent wash water and acid. The resulting slurry is once again dewatered and washed, with acidified wash water, to produce virtually pure lignin cakes”. After the process, the lignin lean liquor is returned to the liquor cycle. The described LignoBoost process is shortly presented in the picture 10. (Valmet. 2017.)



PICTURE 10. Lignoboost process (Valmet. 2017.)

There are couple of considerations that should be taken into account in order to run the process as effectively and economically as possible. The final pH value in the precipitation step in an industrial unit is an important parameter. Also, the amount of precipitation gas used influences the operational cost greatly. The optimized final pH value in an industrial precipitation application is a balance between operational cost and investment cost. The dry solids content of the cake can be increased by applying moderate level of mechanical pressure followed by gas blowing. (Wallmo H. 2008, 13.)

LignoBoost makes it possible to extract lignin from black liquor and to increase the liquor burning capacity of chemical recovery boiler. For example, LignoBoost gives pulp mills new potential and possibilities to increase production, reduce costs and create new sources of income. (Valmet. 2017, 3.)

By removing 25 % of the lignin in the black liquor, the recovery boiler capacity can be increased to allow 20 – 25 % more pulp production. Also, firing lignin in the lime kiln saves up to 50 litres of fuel oil per ton of pulp. This equals 10 000 m^3 of oil for a mill that produces 200 000 tons of pulp per year. Green energy produced from lignin can be profitably exported as process steam or power, or simply sold as fuel in the form of pellets or powder. Lignin is also a good candidate for making specialty chemicals. According to

Valmet, this makes it a very interesting substance for the chemical industry where many companies are looking for renewable raw materials for the production of chemicals. In addition, there have been successful trials at making carbon fibers from lignin. Both exporting lignin as fuel and selling it for further refining give pulp mills opportunities for new sources of income. (Valmet. 2017, 2.)

9 ULTRAFILTRATION TRIALS

The experimental part of this thesis starts with ultrafiltration trials with Valmet’s CR 250/2 filter. The first experiments were done in July in Messukylä’s R&D Center in Tampere and the ultrafiltration tests took time one week. Five different pairs of membranes were tested and results were collected as Excel files. Figures were drawn as well. All the collected results are shown in this chapter.

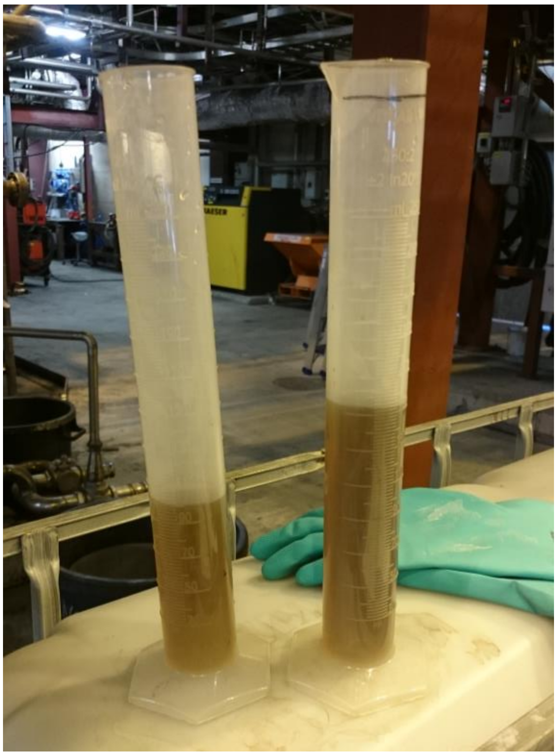
In the table 5 the membrane materials and their molecular weight cut-offs (MWCO) are presented. The table shows the code of the material as well. MWCO is a term used to describe a pore size of a membrane. The smaller the MWCO, the tighter the membrane pore size.

TABLE 5. Membrane materials and their molecular weight cut-offs (Rosenberg P. 2017.)

Code	MWCO, g/mol	Material
P10	10 000	PES. polyethersulfone
P20	20 000	PES
P50	50 000	PES
P	150 000	PES
PS	100 000	PS. polysulfone
RC	500 000	RC, regenerated cellulose
UV150	150 000	PVDF, polyvinylidene fluoride
UFX10	10 000	PS
FS40PP	100 000	FP. fluoropolymer

The MWCO’s tell how tight the membrane is and an example of this is shown in the picture 13. Not all the color variations are seen this clearly, but the picture gives a comparison of different membranes with different MWCO values.

In the picture 11 the measuring glasses are presented. Both permeate flux capacities (upper and lower) were measured by hand with these measuring glasses. Usually the test took one minute at a time and it was taken approximately every 10 to 30 minutes during the tests.



PICTURE 11. Measuring glasses after measuring permeate flux capacities

The used trial layout is shown in the picture 12. The CR 250 filter is placed on the right side and the used container is placed on the left side. All the pipes are on their place. There was also a washing container filled with water but it is not presented in the picture.

PICTURE 12. The trial layout and CR 250 filter during the first week of July in Messukylä

9.1 Trial stages

The trial consists of a couple of different phases. First, the membranes are placed into the CR 250 filter. Then, warm water is run through the system for a while and the capacities are measured by hand. Usually in this phase the capacities are quite high since there is not much to filter. Next, the lignin slurry is run through the system. This phase is marked on the figures as “Recycling with lignin slurry” or simply “Recycling”. Recycling is continued for a good while and capacities are measured every 10 to 30 minutes if possible. After recycling (when the results are steady), concentration phase begins. Now the fluxes are guided to a separate container, out of the system. When the input container starts to get empty, recycling is started again. After a while, dilution phase begins followed by rinsing and washing stages. Washing stage includes washing with soap mixture: it is washed until the foam disappears. Again, the capacities rise when water is run through the system. It is normal if the capacities change between the recycling and concentration stages. Decreasing values in the capacities are usually caused by clogging of the membranes. The tighter the films, the lower the capacity depending on the temperature and pressure.

The capacities are measured by hand during the trial, this is explained and shown in the picture 11.

9.2 Results

The results of the trials are shown in this chapter as Excel figures. Comparing the results is tricky and it is hard to tell, which one of these membrane combinations is “the best”. However, some comparison is done and the discussion continues in the chapter 10.

In the figure 7 the permeate flux capacities for P and RC membranes are presented. P and RC membranes behave similarly. The flux stays almost the same, between 100 and 200 L/m^{2}h during the whole trial. When water is run through the membranes in the start and in the end, the permeate flux increases in both cases. Overall, the RC values are a bit higher than the P values. However, when water is run through, P values increase above RC value. The maximum P value in the end is about 600 L/m^{2}h. For these membranes, the flux color is quite dark as is seen from the picture 13. Their MWCO values are 150 000 g/mol (P) and 500 000 g/mol (RC), so the membranes are rather open. That explains the dark color.

Valmet

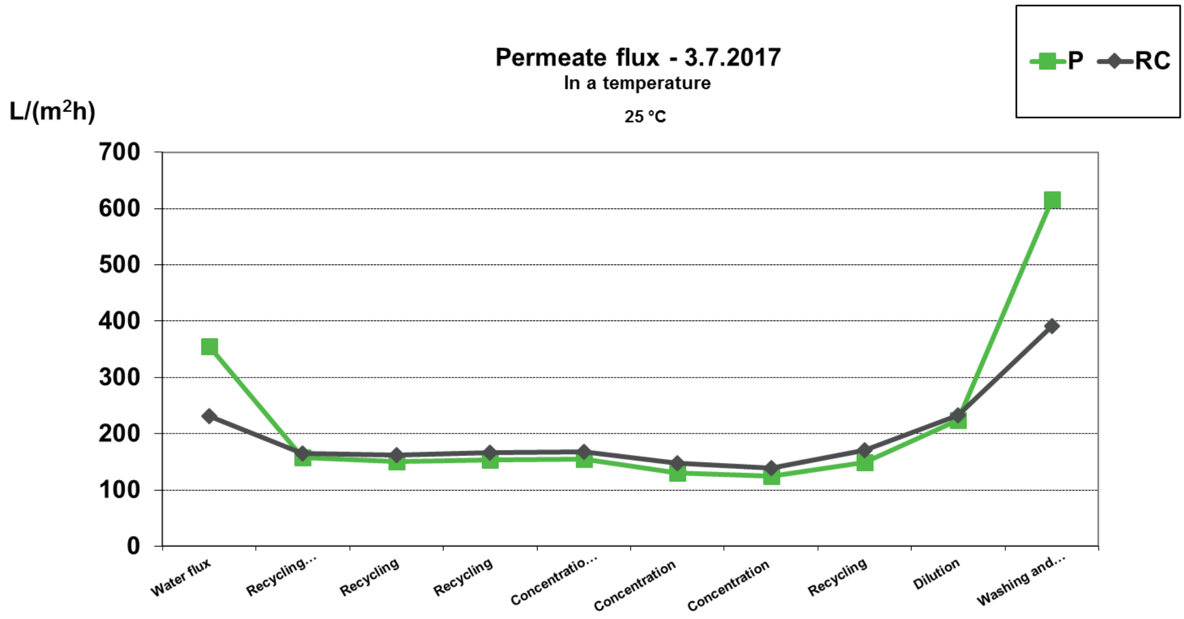


FIGURE 7. Permeate flux for P and RC membranes

In the figure 8 the permeate flux capacities for P20 and P10 membranes are presented. In this case, the capacities vary approximately between 40 and 120 L/m^{2}h. P20 membrane values are constantly higher than P10 values. The difference between these two is about 50 L/m^{2}h in capacity. Altogether, the values follow neatly the same line throughout the test and no big changes are seen. P20’s MWCO value is as low as 20 000 g/mol and P10 is 10 000 g/mol. Therefore, the membranes are quite tight and hold most of the bigger particles in them.

Compared to the previous figure, figure 8's flux capacities are much lower due to the much tighter membranes. These two permeate fluxes are compared in the picture 13.

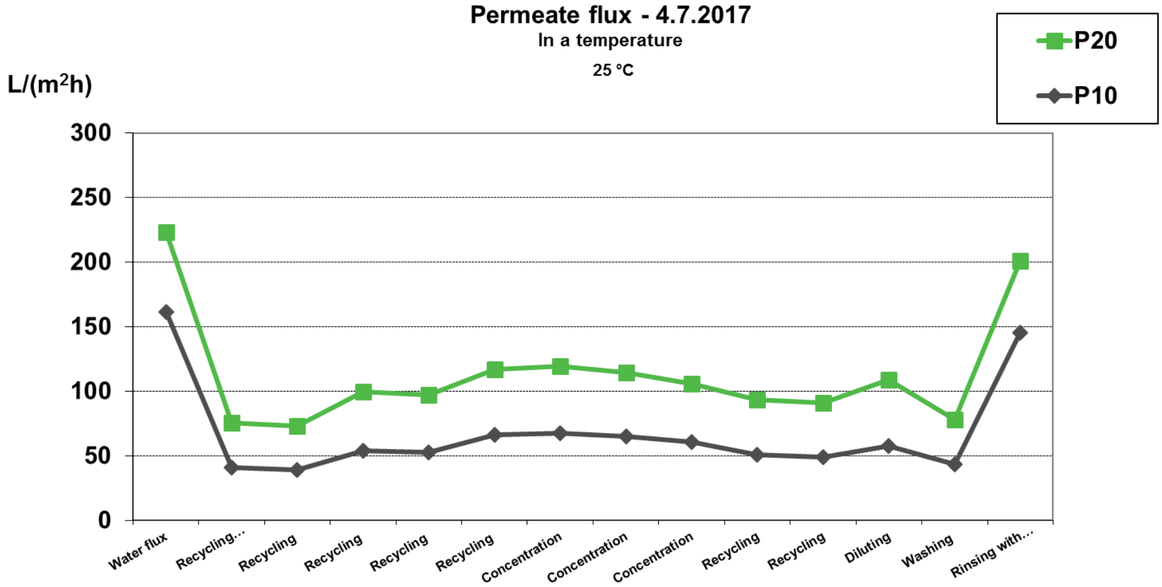


FIGURE 8. Permeate flux for P20 and P10 membranes

PICTURE 13. Permeate fluxes taken from the lower and upper fluxes on 3. and 4.7.

As is shown in the picture 13, the permeate fluxes' colors vary a lot. On the right side is fluxes after filtrating with membranes P20 and P10 and on the left side fluxes after filtrating with membranes P and RC. As is seen on the table 5, the MWCO's are different for these membranes and P20 and P10 membranes are a lot tighter than the membranes P and RC. Therefore, the color is much lighter on the right side and the capacities too were lower compared to the P and RC membranes.

In the figure 9 the permeate flux capacities for PS and UV150 are presented. In this case the values drop from the beginning until the end. The capacities vary from 60 to 275 L/m^{2}h so the range is quite vast. Compared to the two previous figures, this one is exceptional. Both membranes are rather open, PS having the MWCO value 100 000 g/mol and UV150 having the value 150 000 g/mol. The permeate flux capacities are quite high, which is explained by the high MWCO values.

The UV150 values are constantly higher than the PS values, which is easily seen from the MWCO values as well. The membranes seem to get clogged slowly during the trial since the values drop throughout the trial all the way from the beginning to the end. In the beginning the values are about 250 L/m^{2}h and in the end, they are only around 100 L/m^{2}h. This is a rather big jump in the capacities. However, no dramatic changes are seen.

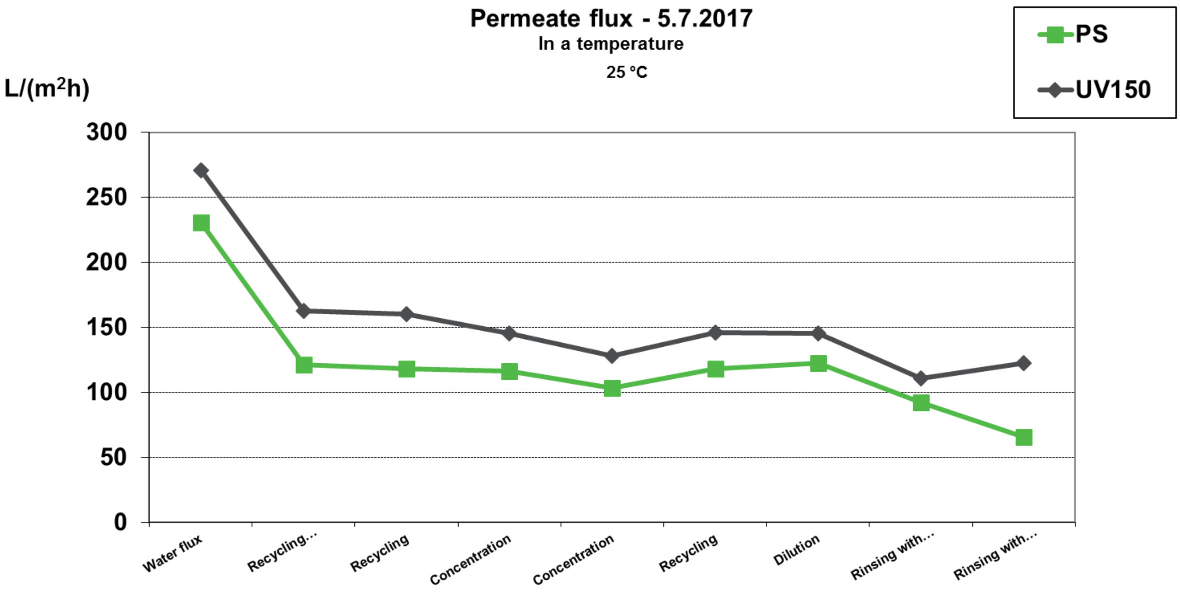


FIGURE 9. Permeate flux for PS and UV150

In the figure 10 permeate flux capacities for UFX10 and PS membranes are presented. This figure is a bit different from the past ones. During the recycling phase, the capacities for both membranes vary between 110 to 200 L/m^{2}h. Then, suddenly, both values drop for a while during another recycling phase and then come back soon after. This might be a measure error: it would explain the drop from 180 to 75. In this trial, the pressure was changed from 1 to 1,5 and 2. This was done by adjusting the pump or valve by hand and it may have caused the error. For example, the valve might have been adjusted too tight by hand and then it is loosened until the values rise to the normal level. The values raise again in the end when the washing and rinsing take place.

However, the permeate flux capacities are quite high in both membranes. They don't vary a lot, but PS values stay lower than UFX10 values throughout the trial. UFX10's MWCO value is only 10 000 and for PS the value is 100 000 g/mol. Therefore, there should be at least some difference in capacities between these two. Altogether the values seem to raise a little from the beginning until the end so no clogging is detected.

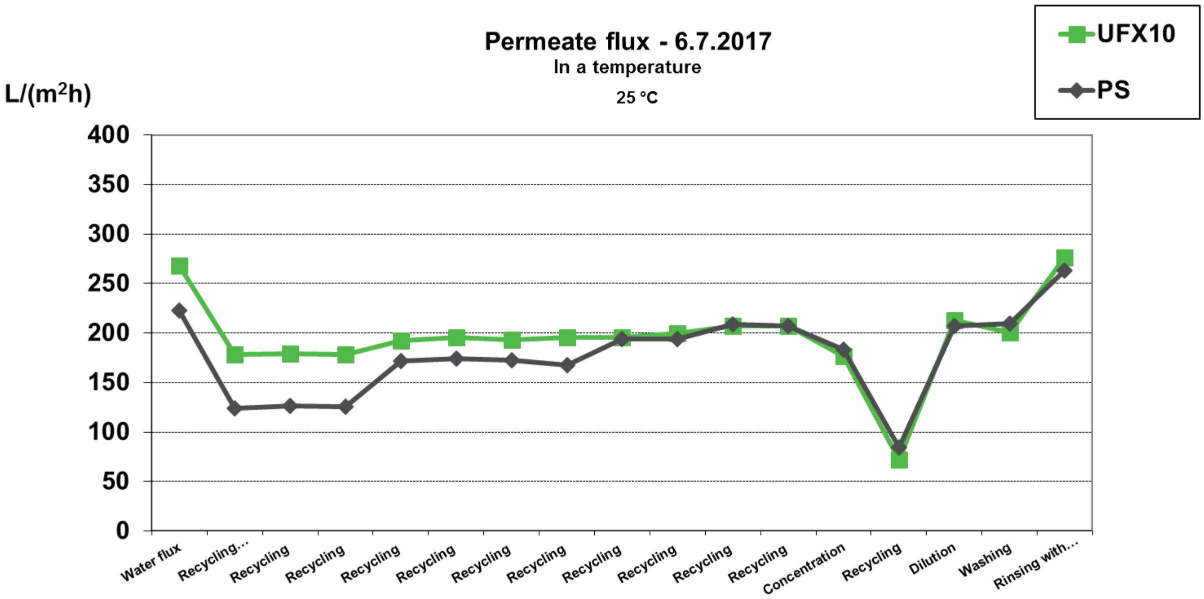


FIGURE 10. Permeate flux for UFX10 and PS membranes

In the figure 11 the permeate flux capacities for FS40PP and P50 membranes are presented. They both follow an almost straight line in their capacities. P50 values are about 50 L m^{2}h lower than those for FS40PP. FS40PP values are constantly near 150 L/m^{2}h and the P50 values are slightly under 100 L/m^{2}h all the time. Both values decrease a little until the end, but no big changes are seen. The MWCO value for FS40PP is 100 000 and for P50 50 000 g/mol. This explains the difference, though the difference should logically be another way around (P50 at the top, being tighter membrane with a lower capacity).

These two membranes are steady and follow steady lines, maybe some clogging is seen due to the lowering graph lines.

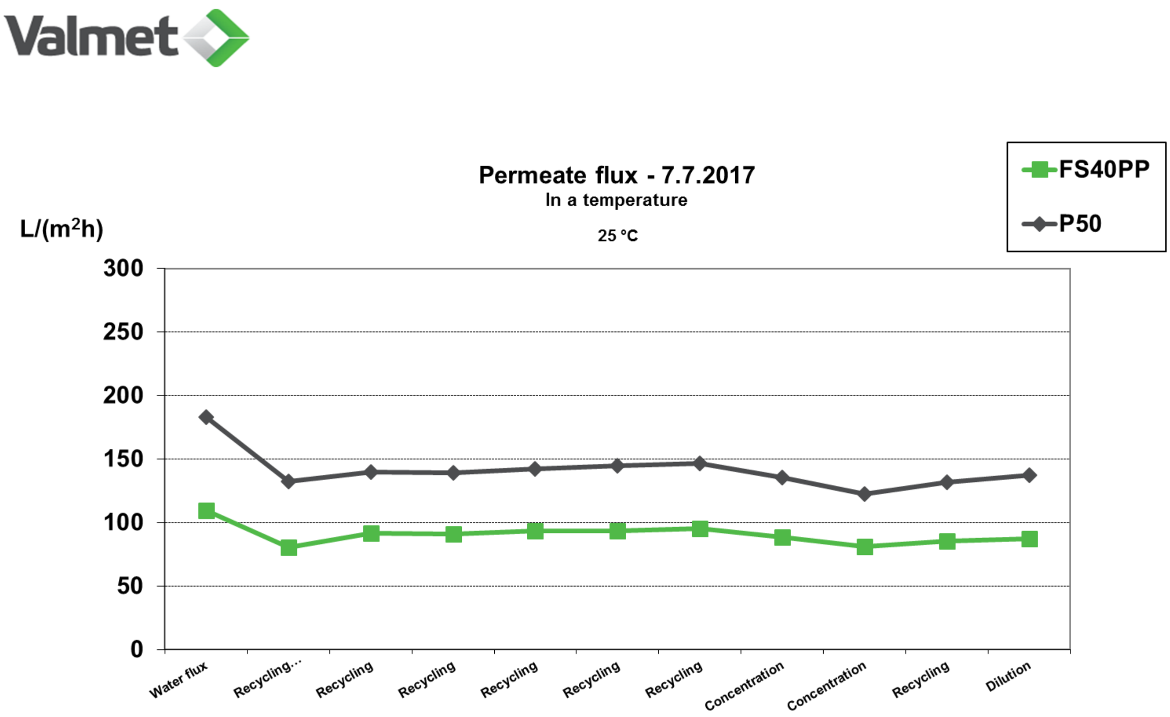


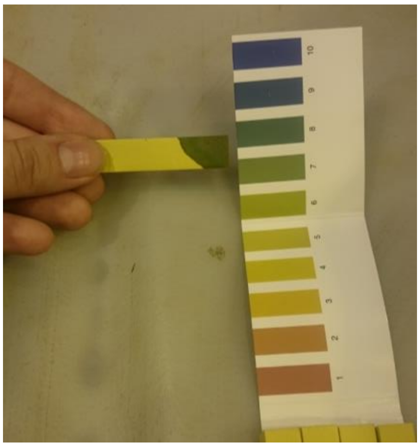
FIGURE 11. Permeate flux for FS40PP and P50 membranes

9.3 Concentration trials and results

From the results of the first membrane trials (results shown above), the most suitable membranes for concentration trials were selected. P and RC membranes were selected to be the most suitable membranes due to their consistent figure (figure 7). It was evaluated that these membranes would be durable enough for longer concentration trials. Also, P10 and P20 membranes were used to compare the results to the P and RC membranes results. These membranes are much tighter and therefore different.

In concentration trials, the same membranes are used unless they start to get clogged. In this case, the membranes are changed. In this type of trial the concentration stage is the only stage, so no recycling or other stages are done. The aim is to see the results faster for the selected set of membranes.

In the picture 14 there is pH paper and the tested value from lignin slurry. The color is somewhere between 7 and 8, which indicates the pH of the matter.



PICTURE 14. Lignin slurry’s pH value

Picture 15 shows how the permeate fluxes were collected during the concentration trials on 23.8.2017. Time and date were marked on the bottles.

PICTURE 15. Permeate fluxes from P10 and P20 membranes

Picture 16 is a picture of dried lignin slurry. This sample is dry and the particles are crystal-like.

PICTURE 16. Dried lignin slurry

The concentration trial was carried out by taking first approximately 70 liters of lignin slurry to a container and more slurry was added if needed over time. The permeate flux rates were measured every 30 minutes as in the first trial. In the end of the concentrating trials, concentrate was collected as a sample.

In the figures, there is a VRF value which is a volume ratio factor. It is calculated by dividing the initial volume by the finishing volume. It is expected to grow exponentially since the finishing volume is reduced over time during the trial.

In the figure 12 there is the permeate flux rate for P10 and P20 membranes. The values vary from 115 l/m^{2}h to 50 l/m^{2}h. Values stay consistent throughout the trial: they go slowly down and only during the washing stage values go up a bit. Pressure in this trial was 2 bars due to the tight membranes. The VRF value is approximately 7,5 at highest and it grows exponentially, which was expected.

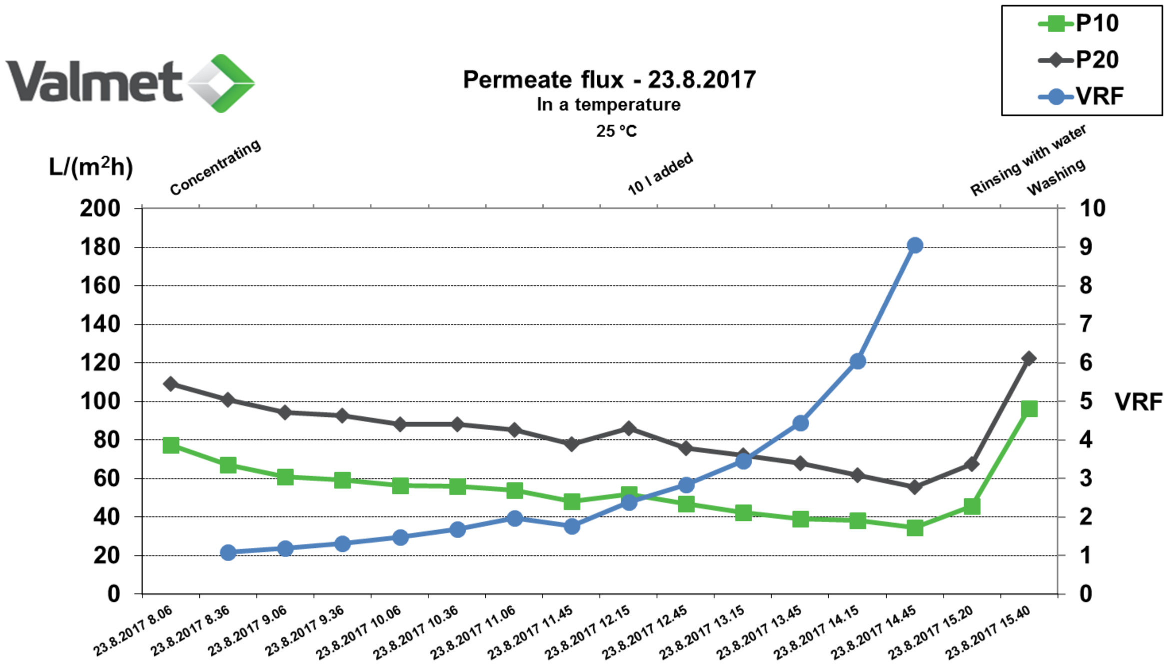


FIGURE 12. Permeate flux and VRF for P10 and P20 membranes

In the figure 13 the permeate flux and VRF values for P and RC membranes is presented. Values for P and RC membranes vary from 160 l/m^{2}h to 50 l/m^{2}h. In this case, the drop is steeper and the values go down more rapidly. P and RC membranes are not as tight as the ones in P10 and P20 trial and that explains the difference between these two. VRF grows exponentially in this trial as well, although there are two higher peaks due to the added lignin slurry.

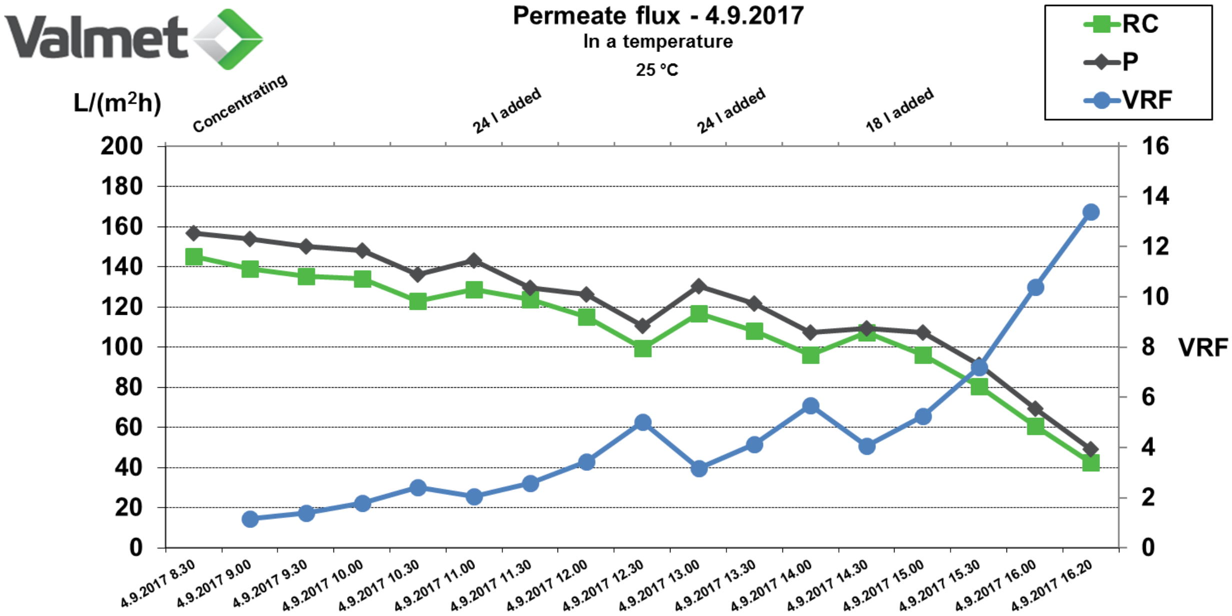


FIGURE 13. Permeate flux and VRF for P and RC membranes

9.4 Laboratory results

Laboratory results were collected in November by Labtium Oy. The results are presented in the table 6, where C refers to concentrate and P refers to permeate flux. The results are surprisingly similar between the used membranes. As expected, the dry solids in the concentrate are much higher than in the permeate fluxes. Also, the dry solids of lignin are the highest in the concentrate. However, the dry solid natrium is almost the same in all the cases so the filtration does not affect the natrium content.

Between the membranes the results don’t vary much, which is somewhat surprising. The results show that only the amount of dry solid lignin is higher in the permeate for P and RC membranes.

The particle size wasn’t tested and it is predicted that the results would vary there more since the pore size for the membranes is different. According to the results, if lower percentage of the lignin is wanted, P10 and P20 membranes should be used. All the other results are almost the same.

The aim of this thesis was to increase the yield in lignin slurry by ultrafiltration technology and in the concentrate this aim is fulfilled as can be seen from the table 6. In the permeate fluxes the solid contents are reduced.

TABLE 6. Laboratory results of the samples (Labtium Oy. 2017.)

	Feed	C (P/RC)	P (P/RC)	P10	P20
Dry solids %	2,1	14,6	0,6	0,5	0,6
Dry solid natrium g/kg	1,66	1,76	1,68	1,69	1,86
Dry solid lignin %	77,8	94,3	36,0	30,8	31,4

10 DISCUSSION

The ultrafiltration of lignin slurry was an interesting study, which results were different than expected. The experimental part showed that P and RC versus P10 and P20 membranes gave different results but the laboratory results were almost the same. The biggest difference is the particle size of the permeate, which is smaller in the case of P10 and P20. Which membranes should be used depends on the wanted results. Also, it takes more time to filtrate with the tighter P10 and P20 membranes which can affect the costs in used process. This might be a significant factor when choosing the suitable membranes. However, both alternatives give reasonable results and should be considered when dry solid lignin needs to be reduced. Both aims of this thesis were achieved: the yield of lignin slurry can be increased and comparison between the membranes was done.

Improvements for the testing can be suggested. First of all, the conditions for the trials should be stationary and for example the temperature of the lignin slurry should be kept the same throughout the trials in order to receive better results. Now the temperature changed throughout the trials and it was noticed that the filtration was faster in higher temperatures.

Also, the particle sizes of the permeates would be interesting to see. The MWCOs are given, but the clear results of the particle sizes from the trials is missing. The particle size is important in the used applications and in the product from the HTC. However, the particle sizes can be held as given in the MWCO table, only the shape of the particles is left unknown.

The reliability of the results is difficult to tell since everything was measured by hand. There are a lot of possible errors in the measurements and it is hard to repeat the trials exactly the same way. The results were also presented by the figures and no calculations was made so the reliability factors can’t be evaluated. This is one improvement point as well. However, there is not much to be calculated from the measured permeate fluxes and the graphs give an interesting presentation on the trials.

Pretreatment methods were discussed in this thesis and these methods could be for example prefiltration, flocculation, coagulation and carbon sorption. Pretreatment methods were not used in this thesis, but they could add some value to the tests in future. More tests need to be done to see if pretreatment would be applicable and useful to the end results.

Altogether, the work was conducted according to the plan and comparison between the membranes was done in two different ways. The laboratory results complete the overall results and give direction when assessing the differences between different membranes. The results can be used in further studies. The advantages for the HTC process is difficult to tell since the target for the HTC is not clear. The ultrafiltration reduces the dry solid contents and the dry solid lignin is reduced so there are some advantages for the HTC as well.

The literature part of the thesis is broad and it gives a good idea how the ultrafiltration works, what are its advantages and what is lignin. The work is completed with suitable photos and tables and additional data is presented when needed. Good amount of references is used as well.

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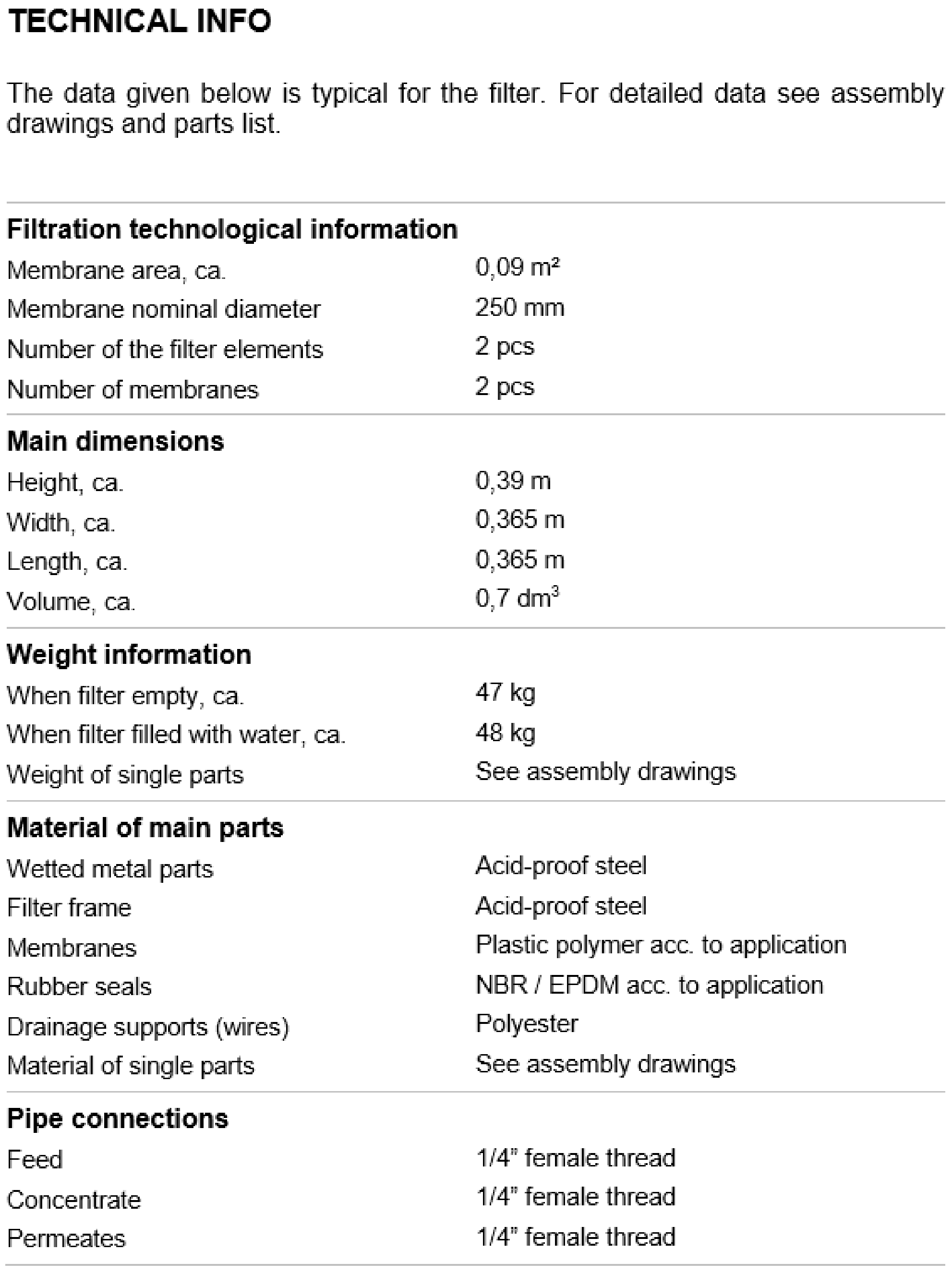
APPENDICES

Appendix 1. Technical info



TECHNICAL INFO

The data given below is typical for the filter. For detailed data see assembly drawings and parts list.

Filtration technological information	
Membrane area, ca.	0,09 m²
Membrane nominal diameter	250 mm
Number of the filter elements	2 pcs
Number of membranes	2 pcs
Main dimensions	
Height, ca.	0,39 m
Width, ca.	0,365 m
Length, ca.	0,365 m
Volume, ca.	0,7 dm^3
Weight information	
When filter empty, ca.	47 kg
When filter filled with water, ca.	48 kg
Weight of single parts	See assembly drawings
Material of main parts	
Wetted metal parts	Acid-proof steel
Filter frame	Acid-proof steel
Membranes	Plastic polymer acc. to application
Rubber seals	NBR / EPDM acc. to application
Drainage supports (wires)	Polyester
Material of single parts	See assembly drawings
Pipe connections	
Feed	1/4” female thread
Concentrate	1/4” female thread
Permeates	1/4” female thread