

Recovery of Dialcohol Cellulose using Micro- and Ultrafiltration Processes

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Abstract

The waste management and production of plastic play a concerning part in global warming and continues to have a negative effect on the environment. A promising strategy to address this challenge is to develop new sustainable materials, to replace current fossil-based plastics. Cellulose is of interest to be used for bio-based materials since it has many desired properties. However, it lacks the formability that petroleum-based materials provide. Converting cellulose into dialcohol cellulose (DAC) is a way to increase the flexibility. DAC is achieved by an oxidation followed by a reduction of cellulose, resulting in an open-ring structure. When producing DAC, it is of interest to increase the yield in the production by implementing a membrane filtration step to concentrate and separate the otherwise lost DAC in the process water. As separation processes commonly account for a major part of the energy and capital cost of a plant, it is of interest to optimise this process to keep costs low whilst still achieving a sufficient separation.

The aim of this thesis was to optimise a membrane filtration process for separating reactants, products, and by-products in process water from the production of DAC. This was done by screening six different membranes, three microfiltration (MF) and three ultrafiltration (UF) membranes, to find the best membrane and optimal operating conditions, based on flux, retention of solutes and fouling. When the optimal conditions and most suitable membrane was chosen, it was examined to what degree it was possible to concentrate the solutes and if the membrane filtration process was affected by using process water provided by Tetra Pak compared to process water produced for this thesis. DAC with different degree of oxidation (DO) was successfully produced for this thesis. The produced DAC used for the concentration had a DO of 58% and a yield of 45%. If using the process water from different reaction steps in the production of DAC affected the concentration was also examined.

The results from the screening showed that an ultrafiltration membrane, ETNA10PP, was the most suitable to concentrate the solutes. The optimal operating conditions were concluded to a cross flow velocity of approximately 0.3 m/s with a transmembrane pressure of 8 bar. These parameters gave a retention of 0.943 when using the reduction step process water from Tetra Pak and a retention of 0.980 when using the reduction step process water produced for this thesis. Further, it was seen that the retention for the process water from the oxidation step was significantly lower than that from the reduction step.

Populärvetenskaplig Sammanfattning

Användandet av fossila bränslen är utbrett och någonting som genomsyrar hela det moderna samhället. Fossila råvaror, som olja, naturgas och kol har många användningsområden och används bland annat vid produktion av plast, som drivmedel för transport och för att producera elektricitet. Att nyttja fossila råvaror är däremot inte oproblemiskt då dessa bidrar till ökande halter av växthusgaser i atmosfären, vilket spår på den globala uppvärmningen. Utöver detta leder förbränning av fossila råvaror till utsläpp av andra skadliga ämnen i miljön, som till exempel kan bidra till försurning av skog och vatten eller orsaka hälsoproblem. För att säkerställa en trygg framtid för både människor och natur är det därför viktigt att minska användandet av fossila råvaror. Ett sätt att göra det är att ersätta fossila råvaror med icke-fossila material med annat ursprung, som till exempel biomassa.

Biomassa finns tillgängligt över hela planeten och har använts av människor som bränsle, byggmaterial och för att göra textilier sedan flera tusen år tillbaka. Biomassa som träd, gräs och andra vedväxter är till största del uppbyggt av någonting som kallas lingocellulosa. Lingocellulosa är ett samlingsnamn för kombinationer av tre komponenter som kallas cellulosa, hemicellulosa och lignin. Respektive komponent har unika egenskaper, men de har alla gemensamt att de är långa kedjor som består av kolhydrater. Den komponent det finns mest av är cellulosa, vilken är uppbyggd av många små sockermolekyler som kallas glukos. Idag utvinns cellulosa till exempel i pappersbruk och vid produktion av textilier. Genom forskning har det visat sig att cellulosa kan användas för att producera plast, vilket är en viktig del i omställningen från fossila råvaror till förnybara.

En plast som kan framställas av cellulosa kallas dialkohol cellulosa (DAC). Denna plast har visat sig ha många bra egenskaper som gör att den potentiellt kan användas för att ersätta viss fossil plast som används idag. När DAC produceras görs detta i en vattenlösning, och för att separera plasten från vattenlösningen används idag ett klassiskt filter som fungerar på samma sätt som en sil. Detta gör att man går miste om en del av den DAC som producerats då den stannar kvar i vattenlösningen.

Målet med det här examensarbetet var att producera DAC och att ta fram en metod för att öka mängden DAC som ges av processen genom att lägga till ett extra filtreringssteg där en separationsmetod som kallas membranfiltrering används. Membranfiltrering är en metod som går ut på att man har ett filter med många väldigt små porer, så att små molekyler (till exempel vatten) åker igenom porerna medan stora (som DAC) hålls tillbaka. För att den här tekniken ska vara så

kostnadseffektiv som möjligt är det viktigt att mängden DAC som går förlorad är så liten som möjligt. Därför lades mycket tid på att hitta de bästa driftsförhållandena för processen genom att variera tryck och med vilken hastighet vattenlösningen rör sig längs membranytan, samt att hitta vilken porstorlek och vilket membranmaterial som fungerade bäst. Efter det användes det optimala membranet och driftsparametrarna för att koncentrera olika typer av vattenlösningar från DAC-produktionen. Det gick bra att producera DAC och det optimala membranet fungerade för att på ett bra sätt koncentrera processvatten från DAC-produktionen, där drygt 90% av materialet i vattenlösningen hölls tillbaka.

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Abbreviations and Symbols

Abbreviations

CFV	Cross flow velocity
DAC	Dialcohol cellulose
DAldC	Dialdehyde cellulose
DO	Degree of oxidation
FTIR	Fourier transfer infrared spectroscopy
HPAEC-PAD	High performance anion exchange chromatography with pulsed amperometric detection
LU	Lund University
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
PWF	Pure water flux
RO	Reverse osmosis
TDS	Total dry substance
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultrafiltration
VR	Volume reduction

Symbols

c_b	Concentration of solute in the bulk solution (mol/L)
c_m	Concentration of solute by the membrane surface (mol/L)
c_p	Concentration of solute at the permeate side (mol/L)
J	Permeate flux (L/m ² h)
k	Mass transfer coefficient (m/s)
P_{feed}	Pressure on the feed side (bar)
P_{perm}	Pressure on the permeate side (bar)
P_{ret}	Pressure on the retentate side (bar)
r	Position along the stirrer radius (m)
R_a	Resistance due to adsorption (m ⁻¹)
R_c	Resistance due to cake formation (m ⁻¹)
R_{cp}	Resistance due to concentration polarization (m ⁻¹)
R_{irrev}	Resistance due to irreversible fouling (m ⁻¹)
R_m	Hydraulic resistance of the membrane (m ⁻¹)
R_{obs}	Observed retention
R_{rev}	Resistance due to reversible fouling (m ⁻¹)
r_s	Total stirrer radius (m)
R_{true}	True retention
V_0	Starting volume (L)
V_p	Permeate volume (L)
μ	Dynamic viscosity (Pa s)
Π	Osmotic pressure (bar)
ω	Angular velocity (s ⁻¹)

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1. Introduction

1.1 Background

Global warming, caused by increasing greenhouse gases is an issue predicted to have a continuously negative effect on the environment. The waste management and production of plastics play an essential role in the greenhouse gas emission concern [1]. The cumulative global production of plastic continues to increase and has to this date exceeded 9 billion tonnes. Almost 80% of the generated plastic by 2015 was accumulated in landfill or the natural environment. If this waste management trend continues, by 2050, we will have 12 billion tonnes of plastic in landfills or the natural environment [2]. A promising strategy to address this challenge is to develop new sustainable materials, to replace current fossil-based plastics. This also gives opportunity to decrease the greenhouse gas emissions that are due to plastic.

Cellulose is a polysaccharide and acts as a major part in plants cell walls, making it the most abundant polymer on earth. It is of special interest as it can potentially be used for bio-based materials [3]. Cellulose has many desired properties, such as high mechanical strength and low oxygen permeability. However, it lacks the ductility and formability that petroleum-based materials provide [4]. For cellulose to become a competitive option on the market it must first be chemically modified to achieve these desired properties. Furthermore, it has been seen that converting cellulose to dialcohol cellulose (DAC) is a way to attain high strength and ductility [5].

DAC is achieved by an oxidation followed by a reduction of cellulose. The reactions are performed in a water solution. The resulting DAC has an open-ring structure at the C2-C3 bond. This open-ring structure leads to more flexibility and different physical properties than that of the usual cellulose with a closed ring-structure [4]. To increase the yield in the production process, the implementation of a membrane filtration step is possible to concentrate and separate the otherwise lost DAC in the process water.

Separation processes are needed in many types of industries and commonly account for a major part of the energy and capital cost of the plant. The choice of processes and at which parameters they run at are therefore of high importance [6]. Membrane filtration is a separation process with lower energy costs in comparison to many other separation processes, however it is still of interest to keep operational costs down. The parameters chosen when optimising such a process must result in a sufficient separation, at a reasonable speed whilst keeping the cost

and energy consumption low [7]. These demands rarely go hand in hand which must be taken into consideration when choice of parameters shall be made.

1.2 Aims and Outline of this Thesis

The aim of this thesis was to optimise a membrane filtration process for separating reactants, products, and by-products in process water from the production of DAC. To do this, six different membranes, three microfiltration (MF) and three ultrafiltration (UF) membranes, were screened to find the one most suitable for this task. The screening was also performed to find the optimal operating conditions for such a process, where transmembrane pressure (TMP) and cross flow velocity (CFV) were varied. The most suitable membrane was identified based on flux, retention of solutes and fouling.

Once the screening had been performed, the chosen membrane was used to concentrate the process water to identify to what degree it was possible to concentrate the solutes. There was also an investigation of how the membrane filtration process was affected by using process water provided by Tetra Pak compared to process water produced for this thesis, as well as varying the process water from different reaction steps in the production of DAC.

2. Dialcohol Cellulose

2.1 Cellulose

As mentioned earlier, cellulose is the most abundant polymer on earth. It is a linear polymeric chain composed exclusively of β -D-glucopyranose subunits. These subunits are linked together by 1,4-glycosidic linkages and form chains typically 8000 to 15000 units long. Due to the strong aggregation of cellulose chains in biomass, it is almost insoluble in most solvents. However, cellulose molecules can be degraded if pre-treated to disrupt fibrous structure [8]. The chemical structure of cellulose is shown in Figure 1. It can be seen how every identical subunit is continuously linked together.

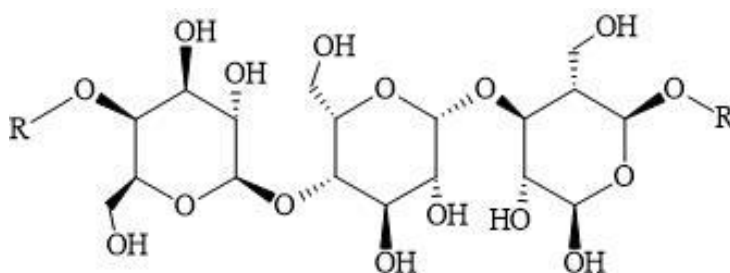


Figure 1. The chemical structure of cellulose showing three subunits linked together.

2.2 Reactions to Produce DAC

DAC is a cellulose-like derivative, that is produced by oxidising cellulose followed by a reduction, see Figure 2. The oxidation performed, cleaves the C2-C3 bond forming dialdehyde cellulose (DAldC) in an open-ring structure. Reducing DAldC gives DAC, also in an open-ring structure [4]. As DAC has an open-ring structure its physical and mechanical properties differ from that of usual cellulose, as it is for example, more flexible. This modification of cellulose is therefore of interest in industrial applications and studies are currently being made to create bioplastics from this material [4].

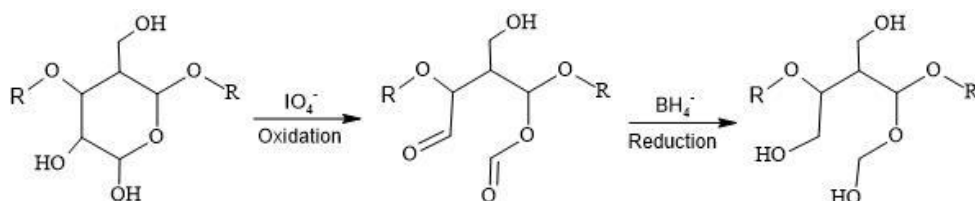


Figure 2. Periodate oxidation of cellulose creating DAldC, followed by borohydride reduction forming DAC.

2.3 Properties of DAC

The properties of DAC and its emerging derivatives are dependent on the amount of aldehyde groups generated along the polymer backbone during the first reaction step, which directly correlates to the degree of oxidation (DO) [9]. The breakage of the C2-C3 bond, see Figure 2, gives DAC a greater flexibility than cellulose, resulting in the surface of DAC easier deforming and adapting to applied forces. Through simulations, it has been shown that the structure has a decreasing crystallinity and interfacial stiffness with increasing degree of modification. In addition, the modified fibres absorb more water compared to unmodified one, which also decreases the interfacial stiffness [10]. The increase of formability in DAC compared to cellulose, whilst still obtaining high strength, makes DAC continuously of interest as these are desired properties [5].

3. Membrane Filtration

3.1 The Basic Principles

Membrane filtration is a pressure driven separation process that utilizes semipermeable membranes to separate solutes of different size. It has been shown in previous studies that membrane filtration can be an efficient method to concentrate different kinds of biomass and cellulosic matter [8, 11] .

The principle behind membrane filtration is letting a liquid flow along a porous membrane, so called cross flow filtration, as illustrated in Figure 3. The size of the pores determines which solutes that permeates the membrane, and which are retained. Because of this, membranes are characterized by the size of their pores. The four main categories, in decreasing pore size, are MF, UF, nanofiltration (NF), and reverse osmosis (RO) [12].

From a membrane filtration process comes two product streams, called the permeate and retentate, shown in Figure 3. The fact that the liquid flows along the membrane surface, and not orthogonally towards it, is advantageous as it results in slower filter cake build-up, which makes it possible to run the process continuously [8].

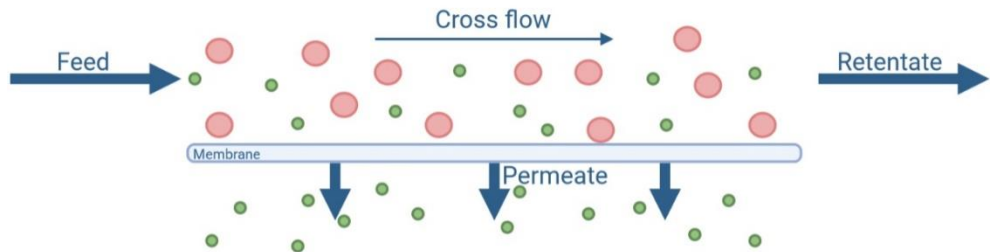


Figure 3. Sketch of the principle behind membrane filtration.

A critical parameter in membrane filtration processes is the flux (J). The flux describes at which rate the liquid permeates the membrane per unit area and can hence be used to partly describe the efficiency of a membrane filtration process. Besides the pore size, the flux is also affected by operating conditions such as transmembrane pressure (TMP), temperature and cross flow velocity (CFV). Equation 1 describes how the flux for pure water is calculated based on TMP, viscosity (μ) and membrane resistance (R_m) [13].

$$J = \frac{TMP}{\mu \cdot R_m} \quad (1)$$

The TMP is calculated based on the pressures in the feed (P_{feed}), retentate (P_{ret}) and permeate (P_{perm}), according to Equation 2 [8].

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

Besides the flux, the retention is an important parameter when determining the efficiency of a membrane filtration process. The true retention (R_{true}), which is a constant membrane characteristic, is defined according to Equation 3, where the concentration in the permeate (c_p) and at the membrane surface (c_m) are used to calculate to which grade a solute is retained by the membrane [14].

$$R_{true} = 1 - \frac{c_p}{c_m} \quad (3)$$

However, in practice it is hard to know the exact concentration at the membrane surface. Hence, the concentration in the bulk solution (c_b) can be used to calculate the observed retention (R_{obs}) instead, as seen in Equation 4 [14].

$$R_{obs} = 1 - \frac{c_p}{c_b} \quad (4)$$

3.2 Flux Reduction

Flux reduction occurs in all membrane filtration processes. It originates from concentration polarisation and fouling. When pure water is filtered, Equation 1 can be used to determine R_m . However, when the liquid contains one or more solutes, concentration polarisation occurs. This phenomenon arises when retained solutes are accumulated in the boundary layer and at the membrane surface, which leads to a decreased effective pressure and concentration gradient over the membrane, resulting in decreased flux, as shown in Figure 4 [8]. The film model in Equation 5 describes the flux when taking concentration polarisation into account, using concentrations at the membrane surface, in the bulk solution, and in the permeate as well as the mass transfer coefficient (k) is used to calculate it [15].

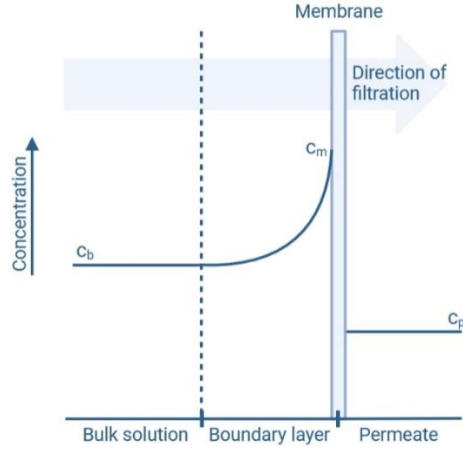


Figure 4. Illustration of concentration polarisation.

$$J = k \cdot \ln \left(\frac{c_m - c_p}{c_b - c_p} \right) \quad (5)$$

In membrane filtration processes with smaller pores, there is a formation of osmotic pressure that decrease the overall TMP, and hence decrease the flux as well. This is relevant mostly for RO and NF filtration processes. Fouling phenomena such as cake/gel formation and adsorption of solutes to the membrane surface are also significant to consider [16]. The resistance in series-model, seen in Equation 6, describes the flux while taking both osmotic pressure ($\Delta\Pi$) and resistances due to concentration polarisation (R_{cp}), cake formation (R_c), and adsorption (R_a) into account [8].

$$J = \frac{TMP - \Delta\Pi}{\mu(R_m + R_{cp} + R_c + R_a)} \quad (6)$$

The four main categories of fouling are adsorption, pore plugging, cake formation and gel formation [16]. It is generally hard to categorize what type of fouling occurs in a membrane filtration process, and hence the categories reversible and irreversible fouling can sometimes be of more practical use. Reversible fouling (R_{rev}) is the resistance acting on the membrane which is eliminated when the solvent is changed to pure water, while irreversible fouling (R_{irrev}) is a resistance which is removable or difficult to remove using a cleaning session. Equation 6 can be rewritten to Equation 7 where the resistances are instead described by reversible and irreversible fouling [16].

$$J = \frac{TMP - \Delta\Pi}{\mu(R_m + R_{rev} + R_{irrev})} \quad (7)$$

Fouling grade is a measurement how much fouling has occurred during a membrane filtration process. It is calculated based on the pure water flux (PWF), before and after the experiment, as seen in Equation 8 [8].

$$Fouling\ grade(\%) = 100 * \frac{PWF_{before} - PWF_{after}}{PWF_{before}} \quad (8)$$

3.3 Membrane Filtration Studies

3.3.1 Parameter Study

A parameter study is a common way to initiate a membrane filtration experiment. It is performed to identify the operational parameters yielding the optimal flux. CFV and TMP are two relevant parameters for such an investigation.

A parameter study is started by setting the highest CFV and the lowest TMP. This is done to prevent fouling [8]. In the setup, both permeate and retentate are recirculated to the feed to keep concentrations constant. The CFV is then kept constant as the TMP is gradually increased, and the flux is logged continuously. This results in a TMP-*J* curve, as seen in Figure 5. This procedure is then repeated for lower CFVs, each generating a new TMP-*J* curve. As seen in Figure 5, the flux in the TMP-*J* curves decrease with decreased CFV. This is because a high CFV limits cake and gel formation, as well as it increases the mass transfer coefficient in Equation 3, thus resulting in a higher flux.

In Figure 5, the different behaviours of a flux from a pure solvent and a flux from a solution with retained solutes are shown. A pure solvent has a linear correlation with TMP, as established in Equation 1, while the solution where material is retained behaves differently in different intervals [11]. For the solutions containing material that is retained, a value called the critical flux is found where the linear correlation between flux and TMP ends. The correlation at low TMP is linear as the fouling effects are not as evident. After the critical flux, the fouling is enhanced, and hence the flux does not continue to increase as rapidly. At a point called the limiting flux, the flux becomes independent of TMP. This occurs due to a formation of a cake or gel at the membrane surface, which itself is a result of saturation of solutes because of the limited permeability of the membrane due to limitations in the convective transport.

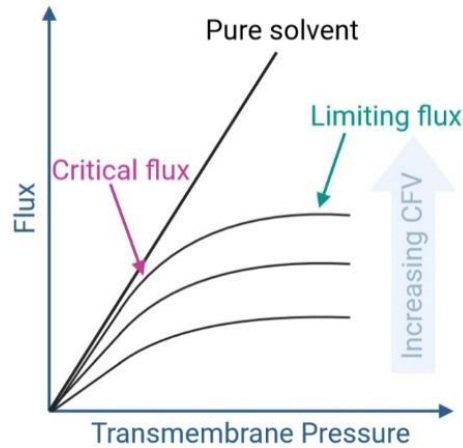


Figure 5. Illustration of a TMP-J curve for a pure solvent and for a solution where material is retained by the membrane for different CFV.

When the critical and limiting fluxes have been found in the parameter study, these are used to determine at what operating conditions the membrane filtration process should be performed. Running the process at the maximum flux, i.e., the limiting flux, results in large amounts of fouling, making the process inefficient. Therefore, a flux close to the critical flux is more beneficial. The threshold flux is a flux between the critical and limiting fluxes, which divides the TMP- J curve into low and high fouling intervals [8]. The threshold flux is used to run a process at as high flux as possible with minimal fouling. It is however time consuming to find, and thus it is common to use the operational conditions of the critical flux instead.

3.3.2 Concentration Study

Once the optimal parameters are identified in a parameter study, the concentration study can be initiated. The concentration study aims to concentrate and separate components in the liquid. To do this, it is possible to use a batch system where permeate is continuously bled off while retentate is recirculated, compared to the system in the parameter study where there is recirculation of all output streams [8]. The concentration study is performed until a certain volume reduction is reached. The volume reduction (VR) is calculated based on the permeate volume (V_p) and starting volume (V_0) according to Equation 9.

$$VR = \frac{V_p}{V_0} \quad (9)$$

4. Materials and Methods

4.1 Production of DAC

4.1.1 Oxidation

23 g of wet cellulose with a dry substance of 32.6 wt% was mixed with 1958 g of water to a 3.6 L bioreactor (Labsfors 5, Infors HT, Bottmingen, Schweiz). 42 g of sodium periodate was then added to this fibre suspension which was gently stirred at 15 rpm. To limit the formation of radicals and unwanted side reactions, the reaction was performed in the dark by covering the reactor. The reaction was performed at room temperature for an oxidation time of 6, 24 or 48 h. The reaction was stopped by filtration through a 40 μm mesh and batch washing of the fibres using 4 L of water [5].

4.1.2 Reduction

After the oxidation the fibres were redispersed in 1870 g of water. The DAldC formed during oxidation was reduced to DAC by adding 3.75 g sodium borohydride. To limit pH increase, monobasic sodium phosphate corresponding to 0.01 M was added together with the sodium borohydride. The reduction time was kept to 4 h and was continuously stirred at 15 rpm in a 3.6 L bioreactor (Labfors 5, Infors HT, Bottmingen, Schweiz). The reaction was then terminated by dead end filtration and batch washing through a 40 μm mesh using 4 litres of water. The reduction took place in room temperature [5].

4.2 Membrane Filtration

4.2.1 Membranes

The membrane filtration experiment setup is based on previous studies by Al-Rudainy [8]. In Table 1, the membranes investigated in the parameter study are presented. All membranes are hydrophobic, and the membrane materials are polysulphone, fluoro polymer, and composite fluoro polymer.

Table 1. Membranes used in the membrane filtration experiments. All membranes are hydrophobic and manufactured by Alfa Laval Nordic A/S.

Designation	Material	Pore size (μm) / MWCO (kDa)	Temperature range ($^{\circ}\text{C}$)	pH range	Pressure range (bar)
MFG1	Poly-sulphone	MF – 0.1	5 – 75	1.5 – 12	1 – 3
MFG2	Poly-sulphone	MF – 0.2	5 – 75	1.5 – 12	1 – 3
MFP5	Fluoro Polymer	MF – 0.5	5 – 60	1 – 11	1 – 3
ETNA01PP	Composite Fluoro Polymer	UF – 1	5 – 60	1 – 11	1 – 10
ETNA10PP	Composite Fluoro Polymer	UF – 10	5 – 60	1 – 11	1 – 10
GR40PP	Poly-sulphone	UF – 100	5 – 75	1 – 13	1 – 10

4.2.2 Process Water

In the study, different process waters were used for different membrane filtration experiments. In the parameter study, process water from the reduction step provided by Tetra Pak was used. In the concentration study, process water from both the reduction and oxidation step provided by Tetra Pak were used, as well as process water produced at Lund University (LU) according to Chapter 4.1 Production of DAC, also both from the oxidation (48 h) and reduction step. The process water from the oxidation step is referred to as step 1 and that from the reduction step is referred to as step 2.

To terminate the reactivity of sodium periodate and sodium borohydride, an addition of ethylene glycol (3.5 wt%) respectively acetone (6.4 wt%) was made to the process water provided by Tetra Pak when reactions were finished. Further, the reduction step process water from Tetra Pak had been neutralised to pH 7. The process water provided by Tetra Pak was produced 7 months prior to the experiments with a DO of 55%.

4.2.3 Parameter Study

Membrane Setup

The screening of the membranes was performed with a setup consisting of a tank combined with an immersion heater (Backer, Elektro-Värme AB, Sjödala,

Sweden). The temperature of the solution was controlled with a temperature control unit (Model MCM, Shinko Technos Co. Ltd, Osaka, Japan). Pressure gauges (DSC40.0AR, Trafag AG, Bubikon, Switzerland) were installed on the feed and retentate side, and the pressure was adjusted using a needle valve on the retentate side. The flow was set with a positive displacement pump (Hydra-cell D25XL, Wanner, Minneapolis, USA) controlled by a frequency converter (ELEX 4000, Bergkvist & Co., AB, Gothenburg, Sweden).

During the experiments, three membrane modules were parallelly connected. The flux was measured using scales (PL6001-1, Mettler Toledo Inc., Ohio, USA), and the CFV measured using a flow meter (FCH-34-PP-Chemical, B.I.O-TECH e.K., Vilshofen, Germany). The TMP was calculated as the average pressure difference between the feed and retentate sides. In all screening experiments, both retentate and permeate was recirculated to the tank to keep concentrations constant. The setup is illustrated in Figure 6 below.

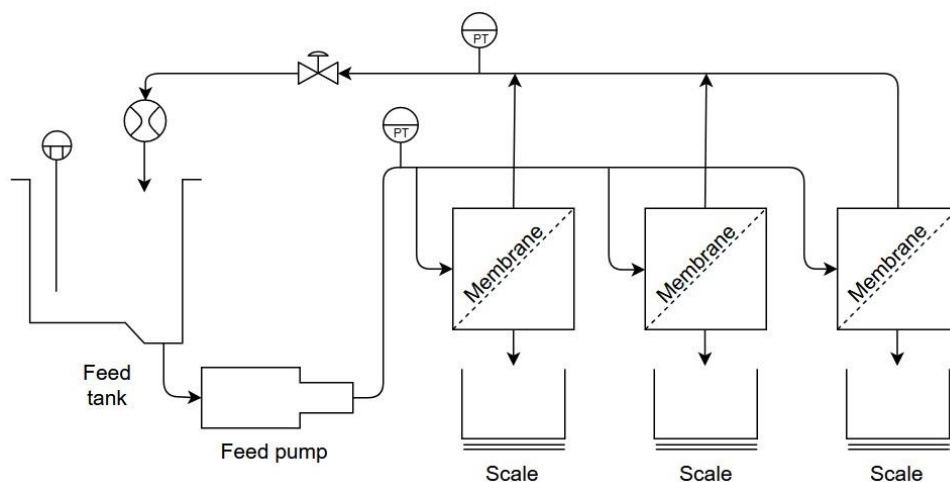


Figure 6. Process setup used in parameter studies.

Membrane Screening

Membranes were placed into the modules and washed using 0.5 wt% alkaline detergent (Ultrasil 110, Ecolab AB, Älvsjö, Sweden) solution for 1 hour at 50 °C, TMP of 1 bar and a CFV of 0.5 m/s. The PWF was measured using deionized water at 30 °C. This was followed by draining the system, for it to be refilled with process water. The highest CFV and the lowest TMP were set. The screening was then initiated by recirculating all permeate and retentate for 20 minutes for the flux to become constant. Following this, the pressure was ramped up every 15 minutes with constant intervals until the membrane's maximum pressure was reached.

Permeate samples were taken at every pressure. The CFV was then decreased to perform the same procedure at CFV 0.4 and 0.3 m/s as well. After this, the modules were drained and refilled with deionized water to measure the PWF. This was followed by cleaning the membranes as when the experiment was started, and a final PWF measurement.

4.2.4 Concentration Study

Membrane Setup

In the concentration study, only the membrane identified as the one yielding the optimal flux and retention was used. A batch system was applied where permeate was continuously bled off. A single stirred cell was used along with a digital pressure gauge (DSC40.0AR, Trafag AG, Bubikon, Switzerland). The pressure was controlled using a valve connected to a nitrogen-gas line and the flux measured using a scale (PL6001-1, Mettler Toledo Inc., Ohio, USA). A magnetic stirrer with a built in heating plate (MR2002, Heidolph, Instruments GmbH & Co.KG, Schwabach, Germany) was used to control the angular velocity of the stirrer according to Equation 10 [17]. In the equation, ω is the angular velocity of the stirrer (s^{-1}), r is the position along the stirrer (m) and r_s the total stirrer radius (m). The process setup is illustrated in Figure 7 below.

$$CFV_{av} = \frac{\int_0^{r_s} 2\pi\omega r \, dr}{r_s} = \pi\omega r_s \quad (10)$$

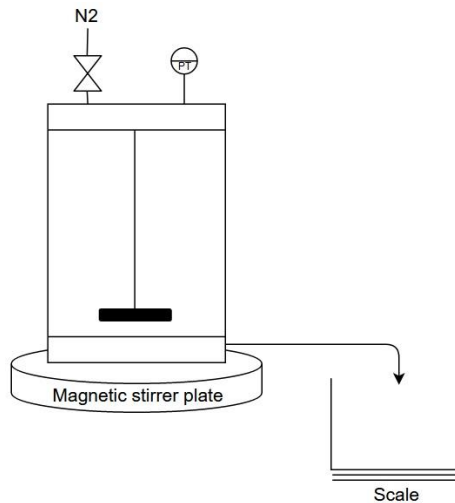


Figure 7. Process setup used in concentration studies.

Study

The membranes were cleaned using 0.5 wt% alkaline detergent (Ultrasil 110, Ecolab AB, Älvsjö, Sweden) solution for 1 hour at 50 °C at 0 bar TMP with a CFV of 0.3 m/s. This was followed by a PWF measurement at room temperature with a TMP of 0.5 bar and CFV of 0.13 m/s. The process water was then added to the vessel to be kept at a stirrer rate corresponding to the optimal CFV found in the parameter study. After this, the optimum TMP found in the parameter was applied. The solution was concentrated at room temperature until a volume reduction of 90% was reached while the flux was logged continuously. Lastly, there was a PWF measurement, followed by cleaning membrane and once again measuring the PWF.

4.3 Analytical Methods

4.3.1 Degree of Oxidation Determination with Titration

The DO of the oxidised fibres was determined by reaction with hydroxylamine hydrochloride [18]. First, a 0.10 M sodium hydroxide solution was prepared. Following this, a 0.25 M hydroxylamine hydrochloride solution was prepared, and the pH was adjusted to 4 with a pH-meter (edge HI2020-02, HannaNorden AB, Kungsbacka, Sweden) using the sodium hydroxide solution. 0.1 g of wet DAldC was stirred with 25 ml of the hydroxylamine hydrochloride solution at room temperature for 2.5 h. The carbonyl content was then determined by titration of the solution back to pH 4 using the sodium hydroxide solution. Each titration was performed in triplicate. Calculations are presented in Appendix A.

4.3.2 Fourier-transformation Infrared Spectroscopy (FTIR)

DAldC samples were dried in an oven at 45 °C for 2 days. A piece of sample was placed over the diamond crystal and its position fixed on a Bruker ALPHA-p FTIR spectrometer (Billerica, MA, USA). Following this, the absorbance spectrum was scanned. The parameters for all measurements included a 4 cm⁻¹ resolution, 4000-400 cm⁻¹ spectral range and 50 scans per sample [18]. Each batch was analysed three times.

4.3.3 HPAEC-PAD

The determination of cellulose and monosugars was performed according to a modified National Renewable Energy Laboratory (NREL) procedure [19]. Samples with a volume of 10 mL were hydrolysed using 750 µL 72% sulfuric acid and autoclaved (Systec DX 150, Wetttemberg, Germany) at 120 °C for 1 h. The samples were thereafter filtered (0.45 µm) to remove acid insoluble compounds and diluted with deionised water before analysis. The remaining liquid was analysed using high performance anion exchange chromatography with pulsed

amperometric detection (HPAEC-PAD), which consists of an ICS-5000+ system (Thermo Fischer Scientific Inc., Waltham, Massachusetts, USA), for determination of monosugars. Sugars and acids were separated on a CarboPac PA1 analytical column (Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA) at 30°C. Deionised water at a flow rate of 1 mL/min was used as eluant, with 0.5 mL/min 200nM NaOH postcolumn addition. The sample injection volume was 10 µL. The calibration standards used were D-glucose, D-galactose, D-mannose, D-xylose, and L-arabinose (Fluka Chemie AG, Buchs, Switzerland).

For the determination of free sugars, the above procedure was performed in the same way, but without the hydrolysing steps.

4.3.4 Total Dry Substance, Ash Content and Total Organic Carbon

To determine the total dry substance (TDS) a heating furnace (Heraeus, Heraeus Holding GmbH, Hanua, Germany) and a precision scale (AND Electric balance ER-120, San Jose, CA). Three millilitre samples were weighed and dried at 105 °C for 24 hours [20]. They were thereafter cooled to room temperature and weighed again to determine the TDS.

Samples were weighed and ashed in a muffle furnace (B150, Nabertherm GmbH, Lilienthal, Germany) at 575°C for 4 hours, after which the ash content was determined from weighing the samples again [20].

The total organic carbon (TOC) content was measured in a TOC analyser (TOC-L CPH, Shimadzu, Kyoto, Japan). Samples were diluted to a desired concentration and filtered through a 0.45 µm filter, if not already filtered by a membrane filtration process. Samples were then placed in the TOC analyser and 0.6 mL of 1 M HCl was added to them. 50 µL of sample was then injected using an autosampler (ASI-L, Shimadzu, Kyoto, Japan). The total carbon (TC) and inorganic carbon (IC) were measured, from which the software calculated the TOC [21].

To avoid any influence of ethylene glycol or acetone in the TOC measurements, a separate TOC analysis was combined with drying liquid samples containing ethylene glycol and acetone in an oven at 105 °C for 2 days. The samples were redissolved to their original volume, filtered through a 0.45 µm filter, and TOC measured again.

5. Produced DAC

5.1 DO, Yield, pH and Residual Components

DAC was produced several times to determine what oxidation time was most suitable. The results are presented in Table 2. In the first batch 24 and 48 h was tested and resulted in a DO of 42% and 56% respectively. In the second batch an oxidation time of 6, 24 and 48 h gave a DO of 14%, 37% and 56% respectively. Although the oxidation time is the same the DO can vary from batch to batch. In addition, a variation of DO can be seen in the different samples taken from the same batch, as the degree of modification is heterogenous throughout the same batch. An oxidation time of 48h was chosen, as although the DO may vary, it gave results closes to the known DO of 55% in Tetra Pak's process water.

The process water from the third batch was used for the concentration study with an oxidation time of 48h. This batch had a measured DO that varied between 56% and 61%, giving an average of 58% and had a total yield of 45%. The yield for the first and second batch were not calculated as the reduction step was not performed.

Table 2. DAC batches, oxidation times and DO.

Batch	Oxidation time (h)	DO (%)
1	24	42
	48	56
2	6	14
	24	37
	48	56
3	48	58

The pH was measured for the process water from the third batch and the process water from Tetra Pak, see Table 3. The variation between Tetra Pak step 2 and LU step 2 is because of Tetra Pak step 2 being processed and neutralised before used in these experiments, as mentioned under Process Water in Chapter 4.

Table 3. The pH values for the different feed samples.

Sample	pH
Tetra Pak step 1	4.0
Tetra Pak step 2	6.9
LU step 1	3.8
LU step 2	9.9

The periodate residue for the third batch was calculated to 24.6 grams, which corresponds to approximately 58% of the initially added 42.2 grams. By assuming

complete reduction of the modified DAldC, the borohydride residue was calculated to 0.63 grams, corresponding to 17% of the total added sodium borohydride. The residual calculations are purely theoretical as the amount of these components in the process water was never measured.

5.2 FTIR

In Figure 8 the FTIR spectra for DAldC can be seen. The blue line represents an oxidation time of 48h and the orange line 24h. The FTIR measurements show how carbonyl groups have been formed with a peak appearing at approximately 1730 cm^{-1} and hydroxyl groups appearing as a broad peak at 3330 cm^{-1} , see the arrows in Figure 8. Further it can be seen in Figure 8 how the hydroxyl group peak is larger for the 24 h sample than the 48 h, but that the carbonyl group peak is the same size. The ratio between these peaks determines the DO. It can therefore be concluded from the figure that the DO is larger for the oxidation time of 48 h.

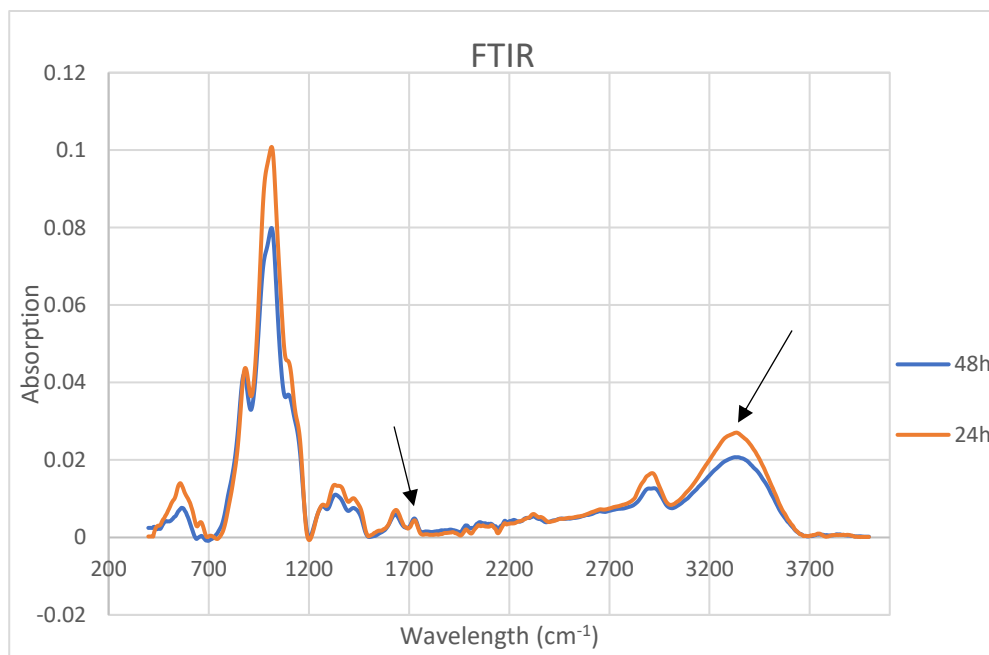


Figure 8. FTIR spectra of sample from oxidation time 24 h (orange) and 48 h (blue), with arrows pointing at the carbonyl peak at 1730 cm^{-1} and the hydroxyl peak at 3330 cm^{-1} .

6. Membrane Filtration of DAC Process Water

6.1 Parameter Study

6.1.1 Microfiltration Membranes

Flux and Fouling

The three MF membranes, all with different pore size, were investigated in the parameter study using process water from the reduction step provided by Tetra Pak, Tetra Pak step 2. The fluxes at different CFV are plotted against TMP for all MF membranes in Figure 9. As expected, the flux increased with increasing TMP as well as with increased CFV for all membranes, and hence the maximum fluxes for all membranes were obtained at maximum CFV and TMP (0.5 m/s and 2.5 bar). The highest flux was observed at the membrane with the largest pore size, MFP5, reaching a maximum flux of 94.2 L/m²h. MFG1 and MFG2 had maximum fluxes of 42.1 and 26.8 L/m²h respectively. Unexpectedly, for the two higher CFVs, the medium pore sized membrane, MFG2, had lower flux than the smallest pore sized membrane, MFG1. However, they both had a similar flux at the lowest CFV. This could be explained by a fast initial increase in fouling for MFG2, decreasing the flux drastically in an early stage, while the increase in fouling was potentially slower for MFG1, making the increase in flux reduction slower. A faster fouling build-up for MFG2 would be possible because of increased pore plugging due to the larger sized pores.

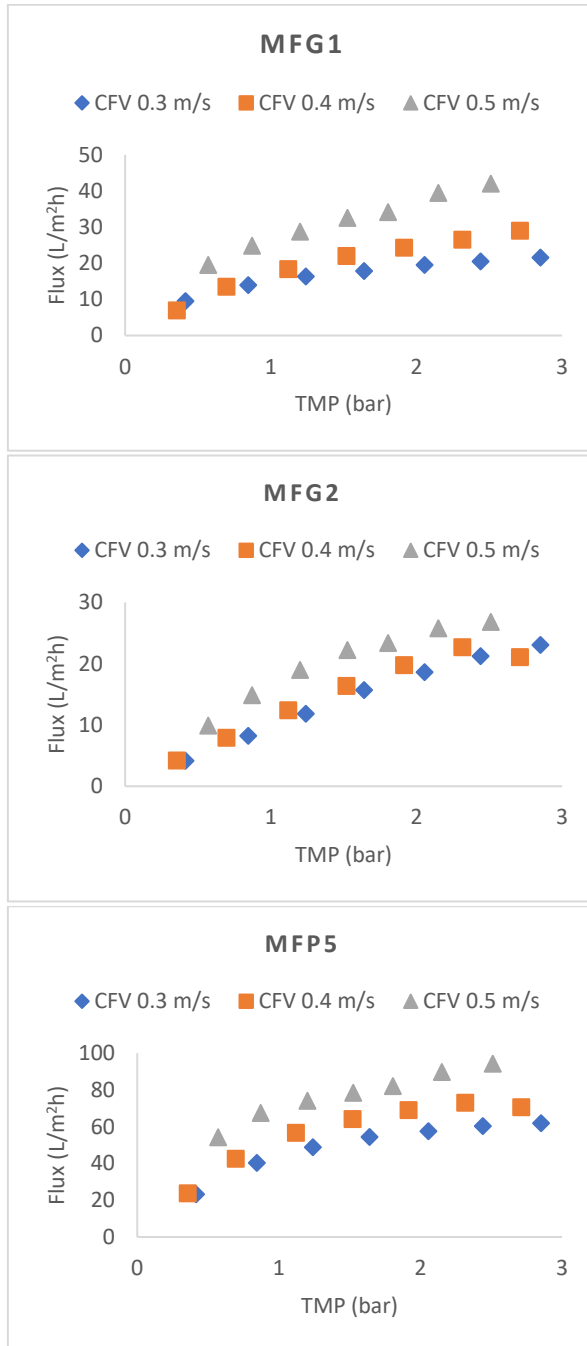


Figure 9. Flux (L/m²h) plotted against TMP (bar) at different CFV (m/s) for MF membranes, MFG1 (0.1 μm), MFG2 (0.2 μm) and MFP5 (0.5 μm).

The fouling grades were high for all MF membranes. MFP5, MFG2, and MFG1 had fouling grades of 83.5, 90.6, and 89.7 % respectively. The high fouling grades could be explained by pore plugging, due to the size of the pores of the membranes. Adsorption of DAC to the membrane surface seems as a less likely explanation, as all membranes are hydrophobic and DAC hydrophilic. As the PWF was measured both before and after the cleaning session at the end of the experiment, it was confirmed all membranes responded positively to the cleaning, as it decreased the sum of the resistances for all membranes (see Appendix B). After the experiments, a thin layer of residual matter was observed on the membranes, see Appendix B.

Retention

The retention of DAC for the MF membranes was calculated from the sugar content measurement using HPAEC-PAD after acid hydrolysis, and the results are shown in Figure 10. The retention did not differ significantly between different CFV for any MF membrane. For MFP5 and MFG2, the retention decreased with increasing TMP. MFP5 had a maximum retention of 0.806 at a CFV and TMP of 0.4 m/s and 0.36 bar respectively, and at the same operating conditions MFG2 had its maximum retention of 0.886. MFG1 had a maximum retention of 0.719 at a CFV and TMP of 0.4 m/s and 2.7 bar. However, the pattern of the retention was not the same as for the larger pore sized membranes, as the retention on MFG1 increased with increasing TMP. It should also be noted that MFG1 had one outlier with significantly lower retention, which is explained by inhomogeneous sample taking for the sugar content measurement.

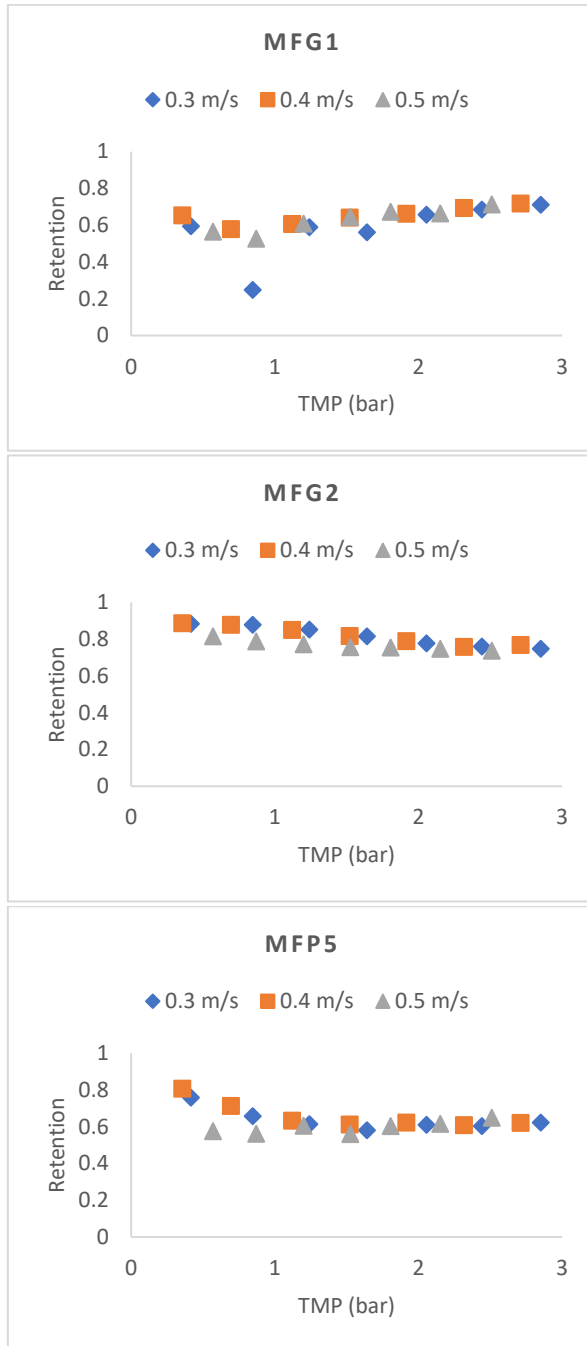


Figure 10. DAC retentions plotted against TMP (bar) at different CFV (m/s) for MF membranes, MFG1 (0.1 μ m), MFG2 (0.2 μ m) and MFP5 (0.5 μ m).

The retention was also calculated based on TDS and TOC. Complete data sets are presented in Appendix B. The maximum TDS retentions for MFG1, MFG2 and MFP5 were 0.367, 0.428 and 0.362 respectively, all occurring at a CFV of 0.5 m/s but at different TMP. The TDS retentions were lower than the corresponding DAC retentions presented in Figure 10 above. This indicates that DAC is retained to a larger extent than TDS, meaning there are significant amounts of other substances in the process water not being retained by the membrane.

The maximum TOC retentions for MFG1, MFG2 and MFP5 were 0.541, 0.578 and 0.557 respectively, which are all lower than the corresponding maximum retentions based on DAC content shown in Figure 10. The TOC retentions decreased with increasing CFV for all MF membranes. This is as expected, as higher CFV reduces concentration polarization effects, and hence decrease the retention. It was also concluded that the TMP did not affect the retention.

In the TOC measurements, it was noted that the experiments yielded unexpectedly high concentrations. The feed TOC concentration was determined to be 32 g/L. This indicated the presence of substantial amounts of other organic compounds than DAC present in the process water. The substances causing this could be acetone and 2-propanol, as acetone was used to stop the reduction reaction in the production of DAC and was added in excess amounts. 2-propanol is the product of this reaction terminating [22]. Hence, the probable high concentrations of acetone and 2-propanol makes it impossible to draw any conclusions regarding the retention of DAC based on these TOC retentions, as they likely correspond better to the retention of acetone and 2-propanol. As acetone and 2-propanol are small molecules, making it impossible for the membrane to retain them, this would also explain why the TOC retentions are considerably lower than the retentions presented in Figure 10.

6.1.2 Ultrafiltration Membranes

Flux and Fouling

The three UF membranes were investigated in the parameter study using Tetra Pak step 2 process water. The fluxes for all UF membranes at different CFV and TMP are plotted in Figure 11 below. As expected, the flux increased with increasing TMP for all membranes. For the two larger pore sized membranes, GR40PP and ETNA10PP, it was observed that the flux also increased with increasing CFV. For GR40PP, no limiting flux was found at the highest CFV, and hence the maximum flux of 112 L/m²h was achieved at a CFV and TMP of 0.5 m/s and 9.29 bar respectively. The maximum flux for ETNA10PP, 83.0 L/m²h, was achieved at the same operating conditions. For the smallest pore size membrane, ETNA01PP, the flux was similar between different CFV. A possible explanation is that the low flux resulted in a smaller filter cake, and hence the size of the pores will alone be the limiting factor to determine the flux. A study conducted on two nanofiltration membranes showed a small or negligible influence on the flux when increasing CFV [23]. As the MWCO for ETNA01PP is 1 kDa, it can be considered and may act closer to that of nanofiltration membranes [24]. The study further showed that the influence of CFV on flux was more apparent with more fouling [23]. The fouling grade for ETNA01PP was low and may therefore further lead to the flux not being affected by the increase in CFV in the same manner as the other membranes were. The maximum flux for ETNA01PP of 42.0 L/m²h was achieved at a CFV and TMP of 0.4 m/s and 9.82 bar respectively.

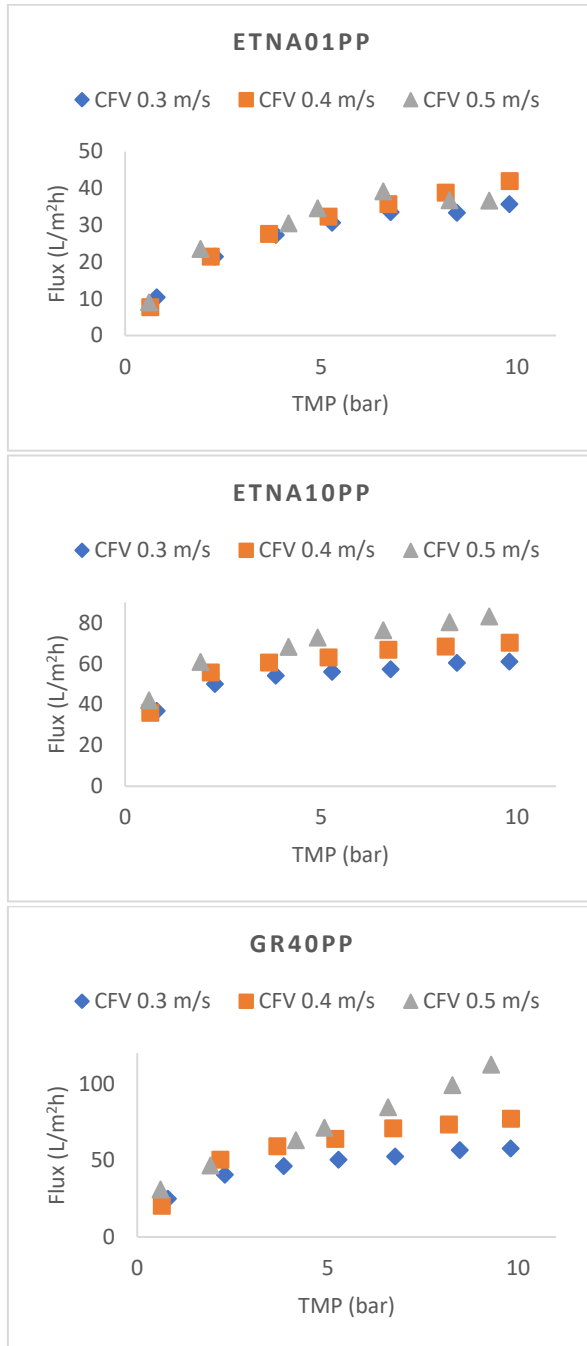


Figure 11. Flux (L/m²h) plotted against TMP (bar) at different CFV (m/s) for UF membranes, ETNA01PP (1 kDa), ETNA10PP (10 kDa) and GR40PP (100 kDa).

Similar to the MF membranes, GR40PP had a high fouling grade, 81.4%. ETNA01PP and ETNA10PP had lower fouling grades of 4.97% and 12.6% respectively. This confirms the earlier stated explanation of high fouling grades occurring because of large pore sizes. Additionally, the cleaning efficiency was confirmed by measuring the PWF after the experiment both before and after the cleaning session. It was concluded the cleaning session was efficient for all membranes as all fouling grades were decreased, as seen in the data in Appendix C, although it had a more significant impact on membranes with high fouling grade. After the experiments, there were no visible matter on the membranes, see Appendix C.

Retention

Due to the reduction agent in the process water reacting with a guard column in the HPAEC-PAD, this method could not be used for the samples from the parameter study conducted with the UF membranes. The samples from the parameter study for the MF membranes were analysed first and therefore used up the guard column which led to the results from the UF samples being undistinguishable, as nothing was protecting the exchange column from the reduction agent. The alternative TOC measurement, with the additional drying step, replaced the HPAEC-PAD analysis.

The TOC retentions (with the additional drying step) for the UF membranes at different CFV and TMP are presented in Figure 12. For all membranes, it was concluded the CFV had little or no impact on the retention. There was also no large variation in the retention as the TMP increased. GR40PP had a maximum retention of 0.911 at a CFV and TMP of 0.4 m/s and 9.8 bar, while ETNA10PP had a maximum retention of 0.972 at 0.5 m/s and 9.3 bar. The maximum retention for ETNA01PP was 0.985, which occurred at a CFV and TMP of 0.3 m/s and 8.5 bar. The feed TOC concentration, after the additional drying step, was determined to be 6.6 g/L.

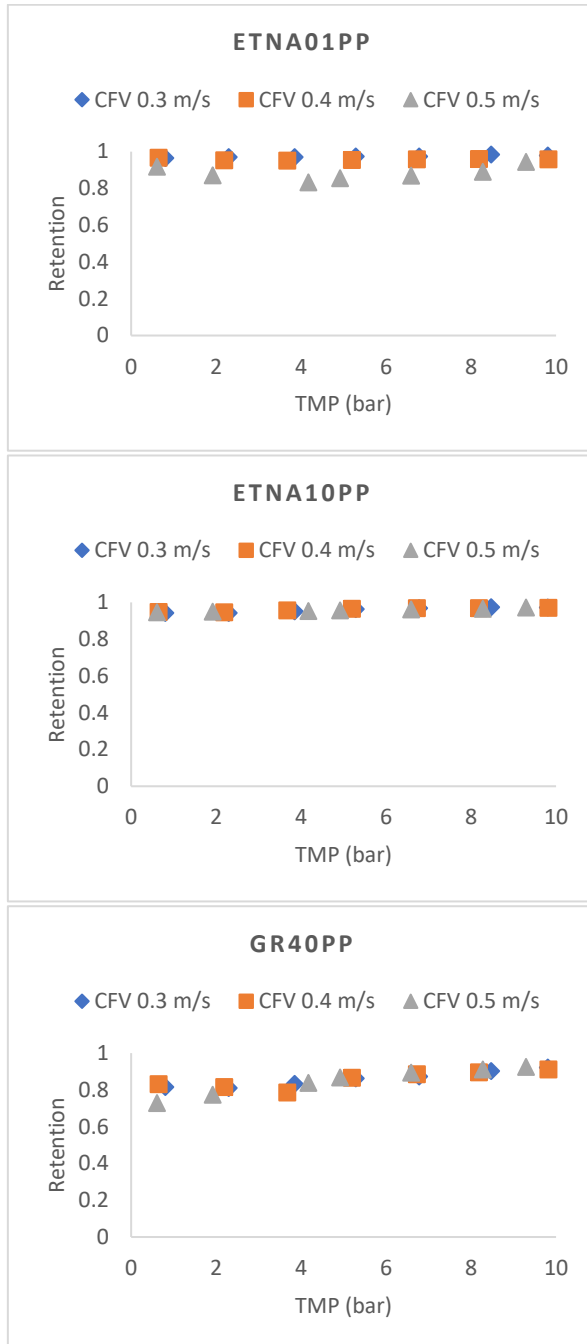


Figure 12. TOC retentions (with additional drying step) plotted against TMP (bar) at different CFV (m/s) for UF membranes, ETNA01PP (1 kDa), ETNA10PP (10 kDa) and GR40PP (100 kDa).

The retention was also calculated based on TOC without the drying step, as well as TDS. The TDS retention was considerably lower than the retentions presented in Figure 12. The maximum TDS retentions for GR40PP and ETNA01PP were 0.299 and 0.464 respectively, which both occurred at the maximum CFV and TMP, 0.5 m/s and 9.29 bar. For ETNA10PP, the maximum TDS retention of 0.371 was achieved at a CFV and TMP of 0.5 m/s and 8.275 bar. For all membranes, a slight increase in retention was observed with increasing TMP, although no large variations occurred. For complete data, see Appendix C.

The TOC retention results without the additional drying step for the UF membranes were similar to the ones from the MF membrane parameter study, where retentions were independent of TMP but decreased with increasing CFV. For complete data, see Appendix C. The feed TOC concentration was determined to be 36 g/L, which is considerably higher than the TOC concentration yielded when the additional drying step was included. This further confirms the presence of acetone and 2-propanol in the process water.

6.2 Concentration Study

For the concentration study the membrane ETNA10PP (MWCO 10 kDa) was chosen at a pressure of 8 bar with a stirrer rate of 250 rpm, which corresponds to a CFV slightly above 0.3 m/s. These parameters were chosen to keep the energy consumption low but still obtain a sufficient flux and a high retention.

6.2.1 Flux

The concentration study done with Tetra Pak step 2 showed a significant decrease in flux in comparison to the parameter study at similar pressure. The flux started at about 20 L/m²h reducing to approximately 7 L/m²h, whereas the parameter study conducted at similar conditions had a flux of 60 L/m²h. This could be due to the concentration study being conducted in a different membrane module that the parameter study was [25]. The step 1 process water both from LU and Tetra Pak had flux that were larger than that of the initial PWF measurement conducted for each study. As can be seen in Figure 13 the step 2 process water has lower flux in comparison to the step 1 process water.

Different runs appear to have different degrees of fluctuations in flux, see Figure 13. This is however not the case, as where the graph shows greater fluctuation the flux average is taken over a shorter logging time. The logging time chosen to measure the average flux was dependent on how quickly the flux decreased and vary from 60 seconds to 15 minutes. It was chosen to do so as the purpose of logging the flux was to see an overall trend rather than knowing the exact value at every given minute.

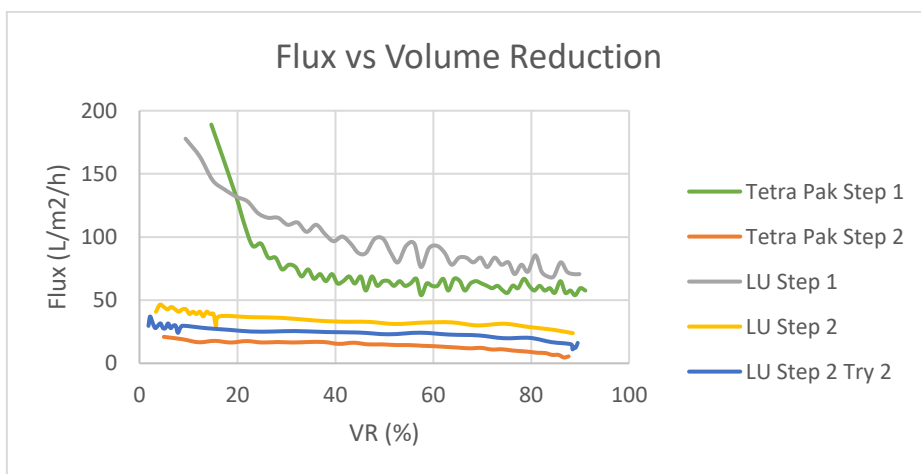


Figure 13. Flux vs VR for the different process waters, at 8 bar TMP, 250 rpm stirrer rate at room temperature.

Continuously, it can be noted from Figure 13 that the volume reduction with step 1 process water is large to begin with, before some sort of cake build up, resulting in the flux stabilising [26]. This trend can be seen with step 2 process water as well, however not as drastically.

The membranes used for the concentration study were the same, however they came from different production batches. When measuring PWF for the different runs in the concentration study, the batch of membrane used was switched once and it resulted in a variation of the PWF even though the conditions stayed the same. It was therefore concluded that this could affect the flux. As mentioned earlier, the change in flux between the parameter study and the concentration study can be because different membrane modules were used [25].

6.2.2 Fouling Grade

The fouling grade was calculated for each run and is presented in Table 4. All runs except when using Tetra Pak step 2 resulted in a negative fouling grade, meaning that the membrane lets through more particles after the process water has been filtered compared to before. The stirrer was suspected to have scratched the membrane for the first run with LU step 2 and both runs with step 1 process water. However, this does not explain why the fouling grade is continuously negative for the second try with LU step 2, as for this run the stirrer was adjusted and made sure not to touch the membrane when stirring. The stirrer presumably had a great affect as the fouling grade does increase significantly between the first and second try with LU 2.

Similar observations of mechanical damage of polymeric membranes have been observed where the active layer of the membrane have been disrupted, resulting in abnormally high permeate flux [27]. It has also been observed that oxidative damage on membranes due oxidants in the process liquid can result in abnormally high permeate flux, which could be a part of the explanation for some of the negative fouling grades as well [27]. An additional reason for the negative fouling could be that cleaning procedure for the membrane was not sufficient.

Table 4. The fouling grade for each run.

Process water	Fouling grade (%)
Tetra Pak step 1	-134
Tetra Pak step 2	13
LU step 1	-58.3
LU step 2	-133
LU step 2 try 2	-19.7

When cleaning the membrane in the parameter study the detergent solution was continuously pressed through the membrane during the entire cleaning time, whereas in the concentration study it was stirred in contact with the membrane and only approximately a third of the initial volume was pressed through the membrane. It is highly possible that a larger volume of the detergent solution needed to be pressed through the membrane and during a longer time. The result of the membrane not being cleaned sufficiently is that it continues to get cleaner during the run as the process water is filtered through it, subsequently increasing the PWF measurement after the run, giving negative fouling grade. This explanation is further justified as initial cleaning of membranes in previous studies have been concluded to give increased permeability of the membranes after the filtration session as well [28].

6.2.3 TOC

The total organic carbon was measured for feed, retentate and permeate from all runs. The results can be seen in Table 5. The Tetra Pak process water was dried and then redispersed before the TOC was measured, whereas the LU process water was measured directly since no acetone or ethylene glycol was added. The runs conducted with step 1 process water have a lower retention and it can be seen how the TOC concentrations are more similar between the three samples from each run, in comparison to those of step 2. This is especially the case for Tetra Pak step 1, which also has the lowest retention by far. Furthermore, the retention for Tetra Pak step 2 is 0.943 whereas LU step 2 has a retention of 0.980. Although the process was optimised with Tetra Pak step 2, this shows that the filtration works sufficiently for process water from freshly produced DAC when observing retention only.

The TOC values from the parameter study for the same membrane at similar pressure and corresponding CFV had a retention value of 0.973 and a measured concentration in the permeate of 174.5 mg TOC/L. The retention for Tetra Pak step 2 in the concentration study was 0.943, which is slightly lower than the value from the parameter study. The measured concentration in the permeate is significantly larger with a value of 1 430 mg TOC/L in the concentration study. The feed concentrations are however relatively similar with a value of 6 080 mg/L, in the concentration study, and 6 560 mg/L, in the parameter study.

Table 5. TOC values for all the samples from the different process waters in mg/L and the corresponding retention.

Process water	Feed (mg/L)	Retentate (mg/L)	Permeate (mg/L)	Retention
Tetra Pak step 1	11 200	12 100	9 900	0.146
Tetra Pak step 2	6 080	43 900	1 430	0.943
LU step 1	174	972	85.8	0.850
LU step 2	1 000	6 620	420	0.890
LU step 2 try 2	1 030	9 060	101	0.980

The retention increased between the two runs conducted on LU step 2 process water, going from 0.890 to 0.980. The run was redone because of suspicion of the membrane being scratched. Due to the increase of the retention, this is presumably the case. The same suspicion was had for both runs with step 1 process water, but there was not enough time to redo these experiments. It is therefore reasonable to believe that the retention can increase for these two runs as well. The scratching of the membranes is most likely due to the stirrer not being fully secured, resulting in it touching the membrane whilst stirring. In Appendix D pictures of the membranes after a conducted concentration study are presented. It is especially clear in the picture of the membrane from the run with LU step 1 that the membrane is scratched. It was also considered that periodate and borohydride, used as the oxidizing and reducing agents during production of DAC, reacted with the membrane.

Before running the samples in the TOC, the retentate and feed were filtered, to avoid large particles destroying the machine. This can however affect the results as the amount of removed particles is unknown. It is therefore probable that the feed and retentate samples have an actual TOC value that is greater than the measured one. The filtering of LU step 2 retentate was especially challenging and only a small amount made it through the filter, whereas the other samples were easily filtered. It is accordingly assumed that the largest difference in measured TOC and actual TOC will be for the LU step 2 retentate.

6.2.4 TDS

The TDS for each sample in every run can be seen in Table 6. The retention was calculated using Equation 4 and taking an average of the feed and retentate concentrations for c_b . These values show that the retention of TDS is lower than that of TOC, see Table 6.

In the parameter study the measured TDS for the same membrane at similar pressure and corresponding CFV was 21.1 g/L in the permeate with a retention of

0.355. Table 6 shows that the retention for Tetra Pak step 2 is 0.690, which is greater than the parameter study retention. This aligns with the results from the TOC, however the calculated retention from TDS differs more from the parameter study.

Table 6. TDS values for the samples from the different process waters in g/L and the corresponding retention.

Process water	Feed (g/L)	Retentate (g/L)	Permeate (g/L)	Retention
Tetra Pak step 1	64.9	226	61.3	0.579
Tetra Pak step 2	35.1	128	25.2	0.690
LU step 1	20.3	20.4	19.9	0.024
LU step 2	7.53	24.1	5.83	0.632
LU step 2 try 2	7.33	30.0	5.00	0.732

The retentate from Tetra Pak step 2 was dried at 45°C for 48 h. After drying, it presented as a clear slightly brittle film, see Appendix D.

6.2.5 Ash Content

Table 7 shows the ash content for each sample from the different process water. Overall, the LU process water had a lower ash content than Tetra Pak process water. The retentate from Tetra Pak step 2 had an ash content of 0.0199% whereas the retentate from LU step 2 contains 0.663% and 0.681% ash respectively. This is a noticeable difference, especially considering that the feed for LU step 2 had a lower ash content than that of Tetra Pak step 2 feed. Furthermore, the differences between feed, retentate and permeate samples is smaller for the step 1 process waters than step 2. For the LU process water, the ash content for the retentate is larger than the feed, whereas the opposite occurs for Tetra Pak process water.

A reason for this may be that the conditions for the concentration study were chosen solely based on results from Tetra Pak step 2, resulting in the process being optimised for this process water. The fact that we had a negative fouling grade for all runs except for Tetra Pak step 2, see Table 7, may also influence the ash content. However, ions, which is most of the ash material in the process water, should pass through the membrane. This means that theoretically, we should not notice any larger differences in the ash content for feed, retentate or permeate. The ash content was only measured with one sample for each value, which should be considered. The measurement can be uncertain as a small difference in moisture content gives an amplified effect. The weights measured after the furnace were small, meaning that even a tiny difference has a large impact. Furthermore, the

furnace is not always consequent and it being common that values vary a lot for the same type of sample run with the same programme.

Table 7. The ash content for the samples from the different process waters presented in wt%.

Process water	Feed (wt%)	Retentate (wt%)	Permeate (wt%)
Tetra Pak step 1	3.55	3.49	3.32
Tetra Pak step 2	1.64	0.0199	1.63
LU step 1	0.959	1.04	0.894
LU step 2	0.393	0.663	0.304
LU step 2 try 2	0.340	0.681	0.297

6.2.6 Comparing Tetra Pak and LU Process Water

The feed results from TDS and TOC show the Tetra Pak process water have higher values. This also applies for the ash content results. An explanation for this could be that the LU DAC production gave a higher yield resulting in a cleaner process water. Another reason could be that ethylene glycol was added to the process water received from Tetra Pak to ensure that no further reactions happened, as this process water was from a DAC production conducted 7 months prior to this parameter study and concentration study taking place.

There was a visual difference between Tetra Pak step 1 process water and LU step 1 process water. Tetra Pak's had a brown colour and contained crystal like pieces whereas the LU process water was see-through. The crystals in Tetra Pak step 1 could have resulted in further damaging of the membrane and be an additional reason to why the fouling grade was the lowest for this run.

7. Conclusions

In this thesis the optimisation of a membrane filtration process to separate and purify DAC from process water was examined. The parameter study conducted concluded that UF was most suitable membrane type, and more specifically the membrane ETNA10PP with a pore size of 10 kDa. When choosing the parameters for the concentration study flux, retention, fouling, and energy consumption were considered. The CFV was set to approximately 0.3 m/s with a TMP of 8 bar. These parameters were chosen to keep the energy consumption low but still obtain a sufficient flux and a high retention. The retention for the chosen membrane with similar operating conditions in the parameter study measured at 0.973, from drying and redispersing followed by TOC, which is 0.012 less than the maximum measured retention for all the UF membranes, but the flux was almost twice as large.

The concentration study resulted in a retention of 0.943 when using the same process water as the parameter study. It was seen that different process waters had different retentions and that process water from the oxidation step had a lower retention than that from the reduction step. Furthermore, the process water from the reduction step freshly produced for this thesis gave a higher retention, at 0.980, than that from Tetra Pak.

Additionally, it was concluded that the washing procedure performed before concentrating the process waters during the concentration study was not sufficient as most runs resulted in a negative fouling grade.

DAC with different DO was successfully produced. The DO and yield for the 48 h batch used in the concentration study was determined to be 58% and 45% respectively.

8. Future Work

The DO of the DAC could affect the result of the membrane filtration. Future studies examining what that effect would be and if the fouling degree also is affected should be conducted. Further, a parameter study done on process water from the oxidation step could result in different parameters being chosen as optimal, since DAldC is less hydrophilic than DAC which would affect its affinity to the membrane and therefore fouling degree and flux. The influence of the temperature of the process water was not examined but can affect the membrane filtration. Other parameters such as pH may also influence the outcome.

The amount of periodate left in the LU process water was only calculated theoretically and should be measured analytically to see if these values agree. Continuously, further analysis of the process water would give a greater understanding of its characteristics and conclusions can be drawn on how the filtration process could additionally be optimised. Characterising the process water may also determine what is formed besides DAC, considering the yield.

A techno-economical calculation can be made to get a greater understanding of the process economics and its feasibility to scale up.

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Appendix A

DO Calculations

The determination of DO (mol%) is based on the reaction between DAldC and hydroxylamine hydrochloride. The original pH and concentration of the hydroxylamine hydrochloride solution should be known. When DAldC reacts with hydroxylamine hydrochloride, the aldehyde groups of the fibres are reacted into oximes and HCl is released, which results in a decrease in pH [29]. By titrating the solution back to its original pH using a NaOH solution of known concentration, the amount of HCl released, and hence the number of aldehyde groups, is determined based on the volume of NaOH used for the titration. By also measuring the total weight of fibres after the reaction, DO can be calculated.

The amount of NaOH consumed (n_{NaOH}) was calculated based on the solution's concentration (c_{NaOH}) and its volume (V_{NaOH}) according to Equation A1, and the corresponding number of cellulose units with aldehyde groups (n_{Ald}) was found as presented in Equation A2.

$$n_{NaOH} = V_{NaOH} * c_{NaOH} \quad (A1)$$

$$n_{NaOH}:n_{Ald} = 2:1 \Rightarrow n_{Ald} = \frac{n_{NaOH}}{2} \quad (A2)$$

From this, the total mass of fibres which contained aldehyde groups (m_{Ald}) was calculated by using the molar mass for one cellulose unit with oxime groups (M_{oxime}), 157 g/mol, according to Equation A3. The molar mass of a cellulose unit with oxime groups is used instead of the molar mass for a DAldC unit as the total mass (m_{total}) is measured after the reaction with hydroxylamine hydrochloride.

$$m_{Ald} = n_{Ald} * M_{oxime} \quad (A3)$$

The remaining mass of cellulose that have not been oxidised into DAldC ($m_{cellulose}$) was calculated as presented in Equation A4, and the corresponding number of cellulose units ($n_{cellulose}$) according to Equation A5 using the molar mass for one cellulose unit ($M_{cellulose}$), 162 g/mol.

$$m_{cellulose} = m_{total} - m_{Ald} \quad (A4)$$

$$n_{cellulose} = \frac{m_{cellulose}}{M_{cellulose}} \quad (A5)$$

Lastly, the total amount of cellulose units, both oxidised and un-oxidised, (n_{total}) was calculated according to Equation A6, which then was used to calculate the DO as shown in Equation A7.

$$n_{total} = n_{cellulose} + n_{Ald} \quad (A6)$$

$$DO \text{ (mol\%)} = \frac{n_{Ald}}{n_{total}} * 100 \quad (A7)$$

Appendix B

Parameter Study – MF

Table B1. The sum of the resistances ($\sum_i R_i$) acting in the filtration processes before and after the final cleaning session in the MF parameter study.

Membrane	$\sum_i R_i$ before cleaning session (m^{-1})	$\sum_i R_i$ after cleaning session (m^{-1})	$\Delta\sum_i R_i$ (%)
MFG1	6.80 E+12	2.86 E+12	-57.8
MFG2	3.72 E+13	2.01 E+13	-46.0
MFP5	4.01 E+12	1.92 E+12	-52.2

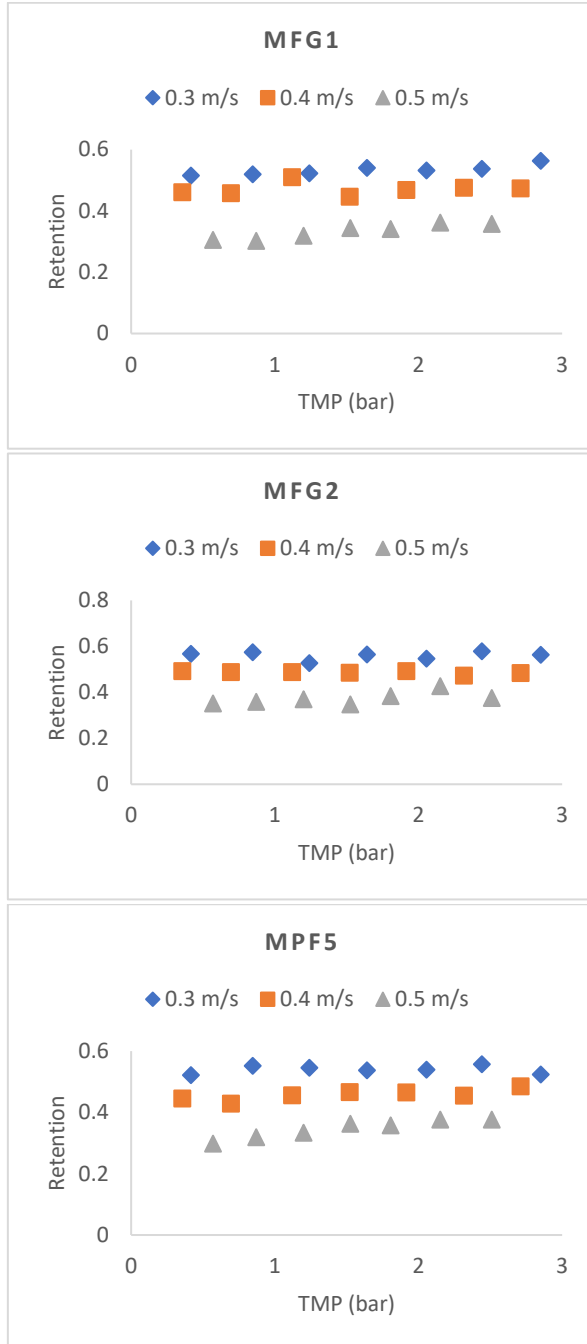


Figure B1. Retentions based on TOC plotted against TMP for different CFVs for MF membranes MFG1 (0.1 μ m), MFG2 (0.2 μ m) and MPF5 (0.5 μ m).

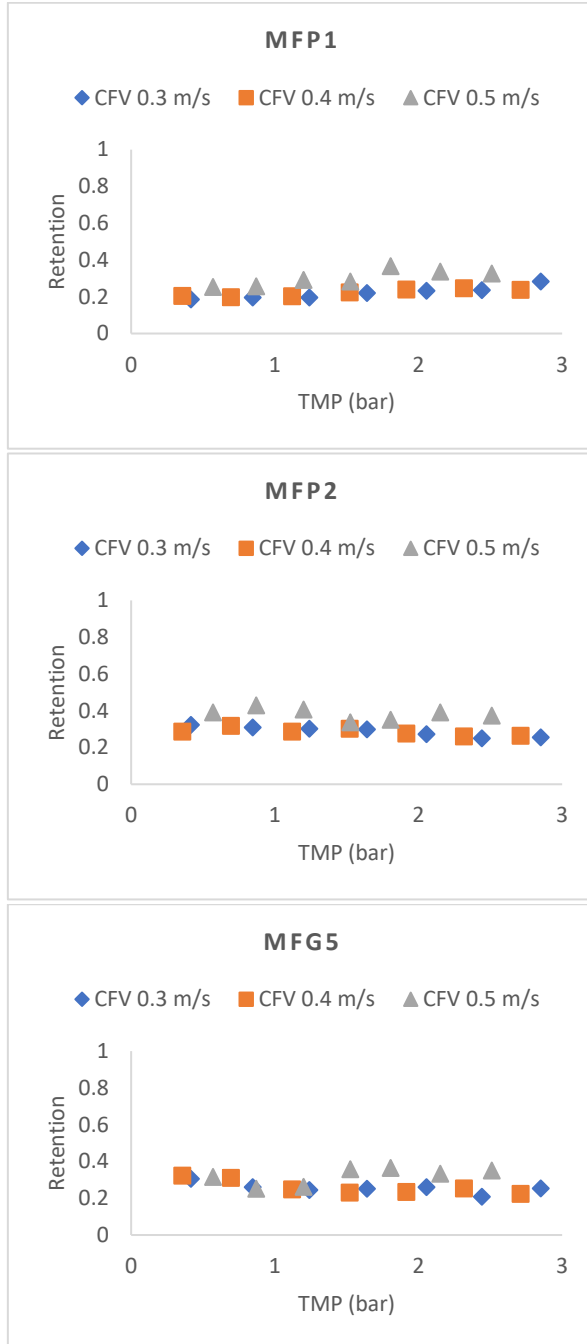


Figure B2. Retentions based on TDS plotted against TMP for different CFVs for MF membranes, MFG1 (0.1 μ m), MFG2 (0.2 μ m) and MFP5 (0.5 μ m).



Figure B3. Picture of MFG1 after the parameter study, where visible matter is present on the filtration area.



Figure B4. Picture of MFG2 after the parameter study.



Figure B5. Picture of MFP5 after the parameter study.

Appendix C

Parameter Study – UF

Table C1. The sum of the resistances ($\sum_i R_i$) acting in the filtration processes before and after the final cleaning session in the UF parameter study.

Membrane	$\sum_i R_i$ before cleaning session (m^{-1})	$\sum_i R_i$ after cleaning session (m^{-1})	$\Delta\sum_i R_i$ (%)
ETNA01PP	1.73 E+13	1.55 E+13	-10.3
ETNA10PP	4.64 E+12	4.54 E+12	-2.19
GR40PP	6.89 E+12	4.44 E+12	-35.6

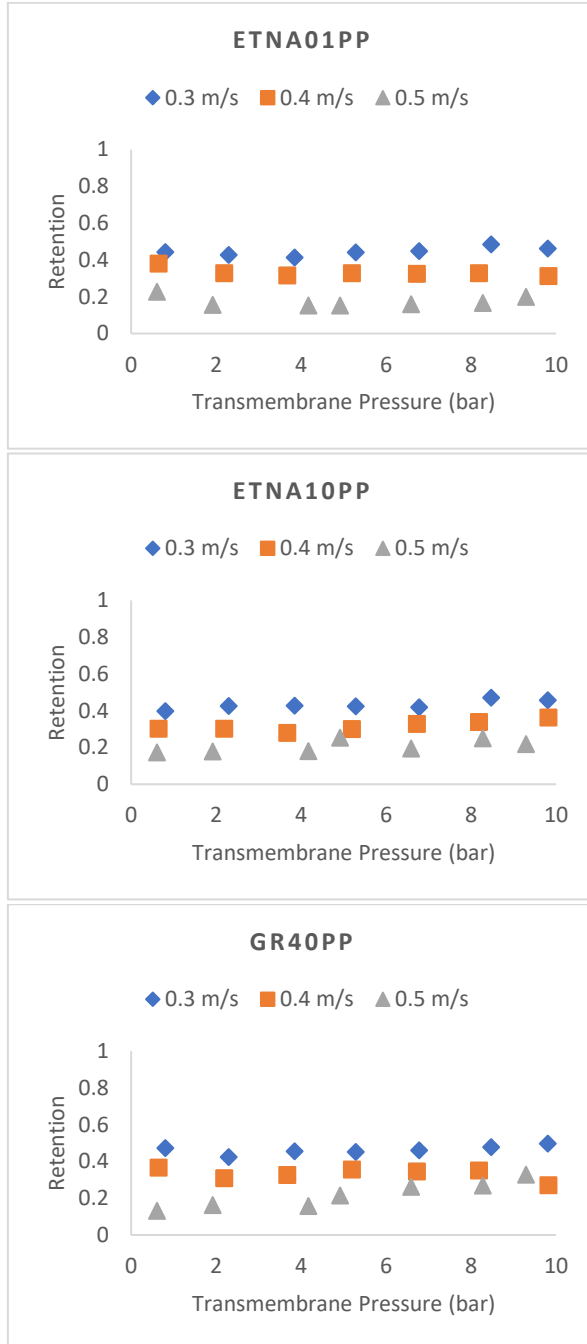


Figure C1. Retentions based on TOC plotted against TMP for different CFVs for UF membranes, ETNA01PP (1 kDa), ETNA10PP (10 kDa) and GR40PP (100 kDa).

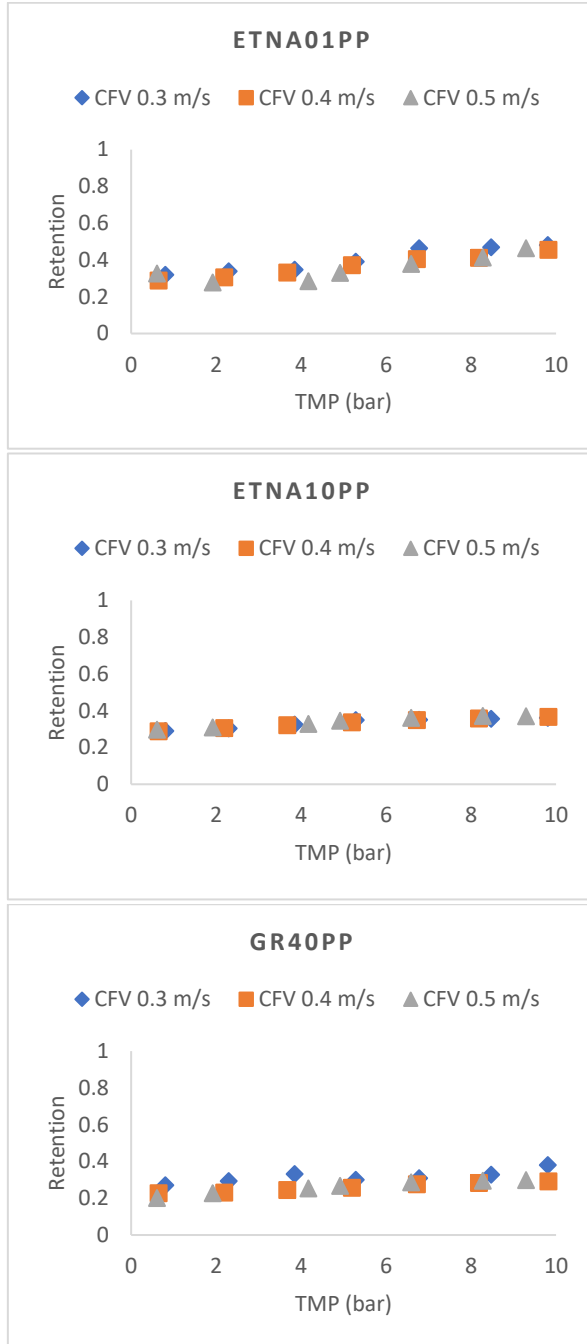


Figure C2. Retentions based on TDS plotted against TMP for different CFVs for UF membranes, ETNA01PP (1 kDa), ETNA10PP (10 kDa) and GR40PP (100 kDa).



Figure C3. Picture of ETNA01PP after the concentration study.

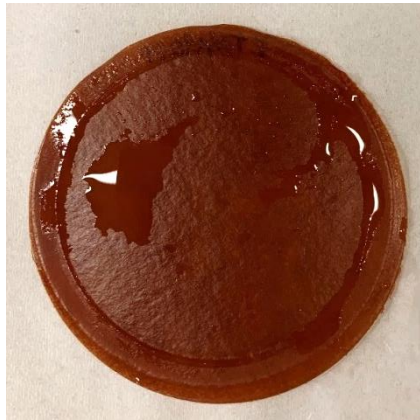


Figure C4. Picture of ETNA10PP after the concentration study.

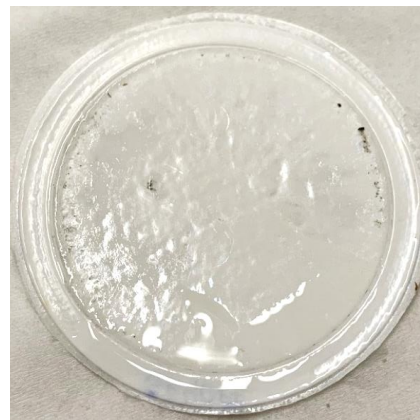


Figure C5. Picture of GR40PP after the concentration study.

Appendix D

Concentration Study

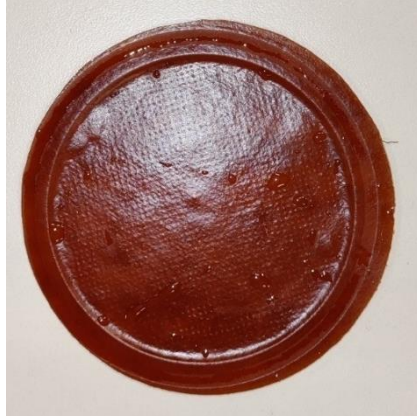


Figure D1. Membrane after filtering Tetra Pak step 2 process water.

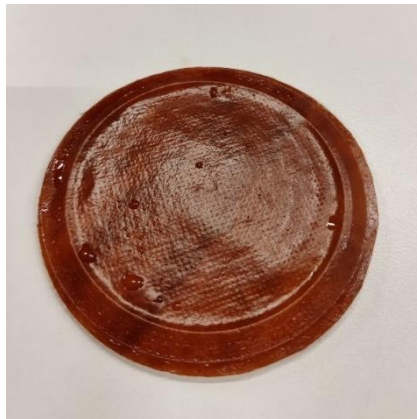


Figure D2. Membrane after filtering Tetra Pak step 1 process water. If looking carefully a scratched circle can be distinguished.

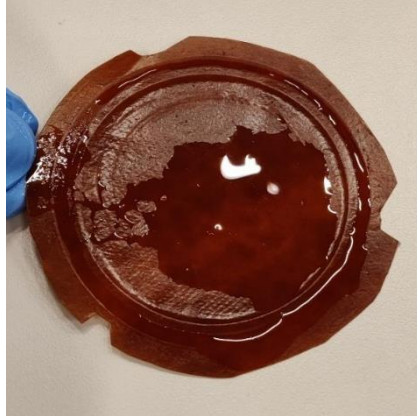


Figure D3. Membrane after filtering LU step 1 process water. It can be seen how the membrane is scratched in a circle with the same diameter as the stirrer.



Figure D4. Membrane after filtering LU step 2 process water, the second try. The stirrer was secured prior to this run, and a scratched circle is not visible on the membrane.



Figure D5. Retentate from Tetra Pak step 2 dried, creating a film.