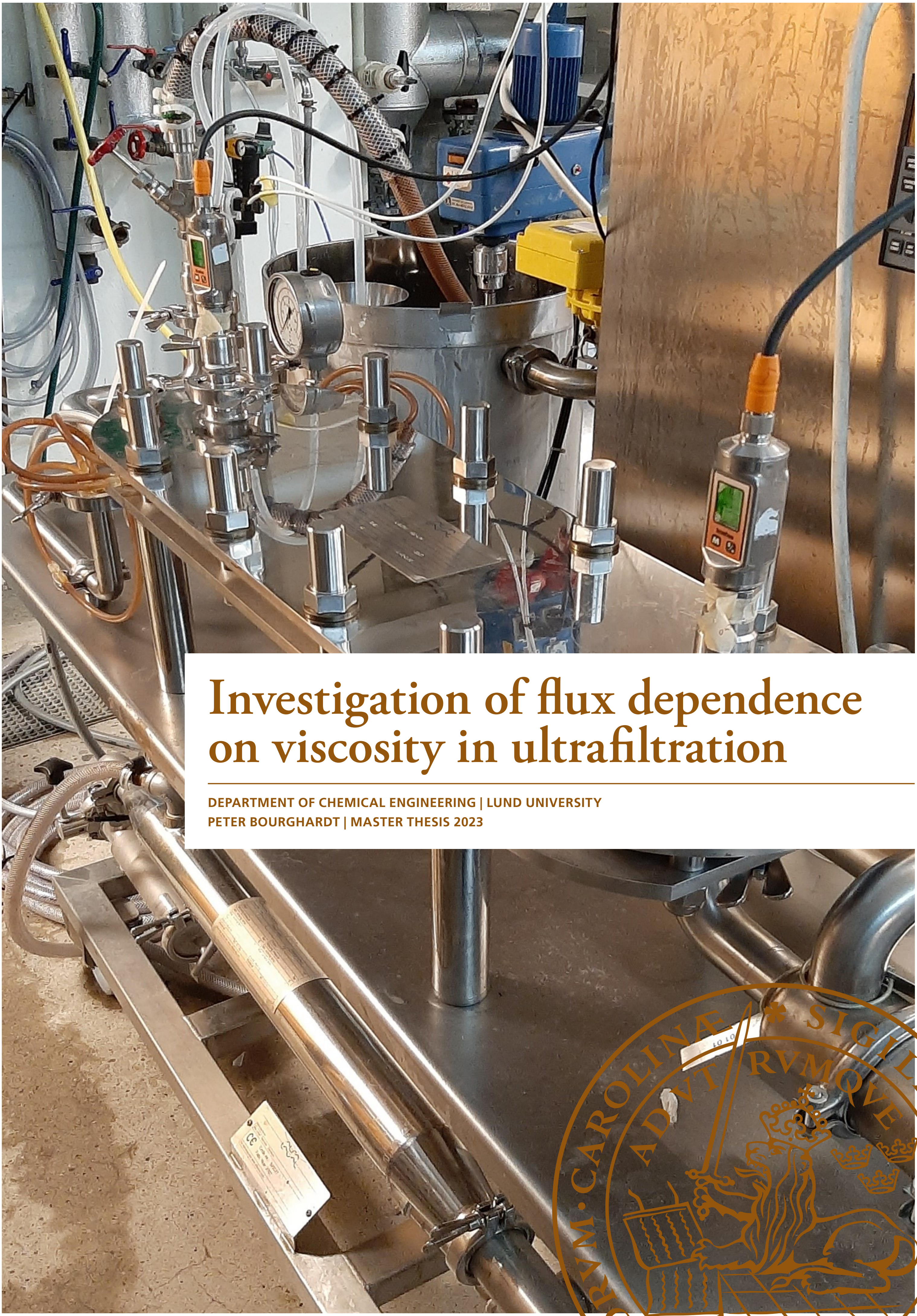

Investigation of flux dependence on viscosity in ultrafiltration

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Investigation of flux dependence on viscosity in ultrafiltration

Master thesis

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Abstract

This project aims to compare the effect of viscosity on flux for high viscosity liquids. The performance of two different viscous solutions was studied in a plate-and-frame membrane module. The solutions used were based on molasses, which is a liquid containing mainly low-molar mass components and konjac glucomannan (KGM) which is a substance with high molar mass. The change of the mass transport through the membrane (flux) during ultrafiltration of molasses and KGM as concentration (dry matter) was increased was investigated. The Alfa Laval RC70PP membrane and the Alfa Laval LabStak M39 equipment were used in the experiments.

Additionally, this study also aims to model and simulate the concentration and viscosity gradient in proximity to the membrane and its effect on the flux by using COMSOL Multiphysics. Simulation of the concentration at the membrane surface is to be used to study different operational parameters effect on the flux at varying viscosities.

In this case, a clear dependence of flux on viscosity was established. For the molasses, there was little retention and the flux was mainly influenced by permeate viscosity. The KGM experiments resulted in permeate viscosity values independent of feed viscosity, the flux was however greatly influenced by increasing hydraulic membrane resistance with higher feed viscosity.

The viscosity effect on flux for molasses was successfully modelled in COMSOL. In the simulation, the concentration gradient in this case was found to have little effect on the flux.

Preface

This master thesis was done at the Department of Chemical Engineering in Lund, Sweden during the spring 2023. The aim was to study the effect of viscosity on flux in ultrafiltration of molasses.

There are several people I would like to thank for their help in making this project possible.

I want to begin by thanking my main supervisor Mikael Sjölin for his support, encouragement and especially for helping to plan and perform the experiments of this study.

I would also like to extend my gratitude to my co-supervisor professor Ann-Sofi Jönsson for her support, many helpful explanations and kind encouragement.

I would also like to thank my co-supervisor Basel Al-Rudainy for his support and for sharing his Comsol knowledge.

I want to thank professor Frank Lipnizki for being the examiner.

I also want to thank the nice people at the department of chemical engineering for their helpful, inspiring and welcoming demeanour.

Lastly, I would like to thank my parents for their support throughout my studies.

Populärvetenskaplig sammanfattning

Jordbruksgrödor används huvudsakligen som livsmedel, men som en konsekvens av en strävan efter ett mer fossilfritt samhälle sker ett ständigt sökande efter andra användningsområden, i synnerhet för biprodukter inom livsmedelssektorn. En sådan biprodukt från sockerindustrin är melass. Melass består mestadels av socker men också av bl.a. andra organiska föreningar och salter, och har traditionellt använts som djurfoder eller för fermentering med mikroorganismer. Ett fortsatt utvecklande av melass som råvara för dessa eller andra syften förutsätter ofta någon som av upprening eller separation av melassen. En metod som då kan användas är ultrafiltrering. Ultrafiltrering är en form av membranfiltrering och som alla tekniska separationsprocesser syftar den till att dela upp ett material i dess olika beståndsdelar. Vid ultrafiltrering sker detta genom att en lösning som innehåller olika lösta ämnen eller partiklar under tryck strömmar längs med eller mot ett speciellt mycket finporigt membran. De partiklar som är tillräckligt små eller har därför lämplig geometri kommer då kunna ta sig igenom membranet medan övrigt material avskiljs. Två aspekter av särskilt stor betydelse när det gäller ultrafiltrering är viskositet, och koncentrationspolarisering. Viskositet är ett mått på hur trögflytande en vätska är och melass med sin tjocka sirapslika karaktär är således ett bra exempel på en vätska med hög viskositet. Koncentrationspolarisering innebär i det aktuella fallet att ett ämne koncentreras i en del av processen, i synnerhet vid membranets yta. Både en hög viskositet och en tydlig koncentrationspolarisering innebär vanligtvis att flödet genom membranet hämmas. Denna studie syftar till att undersöka detta samband vid ultrafiltrering av melass. Melass är ett ämne som består av många förhållandevis små partiklar. Partikelstorleken har stor betydelse vid membranfiltrering. Som jämförelse i denna studie utförs därför även vissa experiment med konjak-glukomannan, som är ett ämne bestående av långa grenade partiklar, inte olik cellulosa.

List of abbreviations

A	m^2	*Area*
C	*g/l*	*Concentration*
C_0	*g/l,*	*Starting concentration molasses*
C_f	*g/l*	*Feed concentration*
C_p	*g/l*	*Permeate concentration*
D_h	*m*	*Hydraulic diameter*
D	m^2/s	*Diffusion coefficient*
h	*m*	*Height*
J	*m/s,* $l/(h\ m^2)$	*Flux*
J_p	$l/(h\ m^2)$	*Permeability*
l	*m*	*Length*
m	*kg*	*Mass*
m_0	*kg*	*Starting mass of molasses*
NF	-	*Nanofiltration*
P	*bar*	*Pressure*
R	-	*Membrane retention*
Re	-	*Reynolds numbers*
R_{tot}	m^{-1}	*Total filtration resistance*
R_f	m^{-1}	*Membrane fouling resistance*
R_m	m^{-1}	*Clean membrane hydraulic resistance*
T	*C, K*	*Temperature*
t	*h*	*Time*
TS	*wt-%*	*Total Solids*
V	*l*	*Volume*
V_0	*l*	*Starting volume*
v_0	*m/s*	*Feed flow inlet velocity*
v	*m/s*	*Velocity*
V_f	-	*Viscosity retention factor*
UF	-	*Ultrafiltration*
μ	*Pa·s*	*Viscosity*
μ_f	*Pa·s*	*Feed viscosity*
μ_p	*Pa·s*	*Permeate viscosity*
ρ	kg/m^3	*Density*
∇	-	*Gradient*

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1. Introduction

Although micro- and ultrafiltration have been for decades established separation methods, mass transfer limitations, which are often related to concentration polarization and fouling, remain the Achilles' heel [1]. Among the main applications of ultrafiltration (UF) is the concentrating of macromolecular solutions such as protein and polysaccharide solutions as well as cell suspensions [2]. Molasses is one such substance, while traditionally used for low value applications, the high sucrose content of molasses means there is a potential to use it for higher value end products. This includes a rising number of biofuels, polysaccharides, oligosaccharides, organic acids, and enzymes produced through the use of microorganisms, finding applications within food, energy and the pharmaceutical industry [3]. Molasses however often require some sort of pre-treatment to support microbial growth [4]. In fact, molasses contains natural components which may inhibit microbial growth, and although this may present a challenge for some applications, they may also act as a natural food preserver [5]. Altogether this makes molasses of interest for applications involving UF.

1.1 Aim and scope

The aim of this study was to examine the effect of viscosity on flux for high viscosity liquids during UF. The main focus of the study was on the behaviour of solutions of molasses, containing mainly low-molar mass components, of varying concentration and therefore viscosities. For comparison, a few experiments were also done using konjac glucomannan (KGM) which is a substance with high molar mass.

Additionally, this study aims to simulate the flux behaviour of molasses as well as the concentration and viscosity profile in the membrane module using COMSOL Multiphysics.

2. Background

The main use for crops is as food, but as a consequence of the drive towards a more fossil free and sustainable society there is an increasing amount of alternative applications for agricultural by-products. There is a broad ambition to gradually phase out fossil energy forms and instead strive for a society based on more electricity. A parallel development is that towards a more energy efficient production of fossil free goods, which improved use of by-products from agriculture and other food industry may be one part of.

Molasses is such a by-product from the sugar industry, containing to the largest part sugar but also other components such as salts, proteins and larger carbohydrates. Being a major by-product of the sugar industry, the total world production is approximately 55 million tons [3]. Molasses is what remains after the last stage of sugar separation when no further sugar can be crystallized. Two important characteristics in molasses are Brix and density, and while these may vary slightly depending on type of molasses, are typically 75 and 1,6 kg/l respectively [6].

The use of the various components usually demands their separation from each other. Molasses is a liquid with high dry matter, but it is usually diluted to be manageable in processes, and can then at a later stage be concentrated again if required. For this use membrane filtration represents a method which is both energy efficient and electricity based. [7]

Membrane processes has been involved with major breakthroughs in various industry branches, including branches such as petroleum, gas, pharmacy, biotechnology, water, wastewater, food processing and medicine. This has led to improvements in general product quality, product yield, new products and decrease in energy consumption. The sugar industry is one of the most energy consuming industries in the food industry, motivating extensive investigation of possible membrane applications within this industry [6]. According to Mousavi et al. research into possible new applications of membrane filtrations within the sugar industry have focused of four different areas: (i) purification of raw syrup, (ii) the concentration of diluted syrup by reverse osmosis, (iii) separation and extraction of colour compounds and (iv) achieving products with high protein percent [6].

While nanofiltration (NF) can be used for purification and desugarization, UF can be more useful when the aim is to separate non-sucrose compounds or macromolecules [6, 8]. These methods lead to a decrease in both energy consumption and environmental impact [6].

Increasing viscosity as the separation continues presents a challenge during membrane filtration since the concentration and thickness of the boundary layer increases which inhibits the mass transport through the membrane as well as centrifugal pumps suffering a decline in performance as viscosity increases [1, 9]. One solution is to apply so called dynamic filtration, where the build-up of a filter cake is counteracted by the use of a rotating disc, or by vibrating the membrane [2]. Molasses, being a liquid of high viscosity, is well suited for examining the effect of viscosity on the mass transport through the membrane (flux) during membrane filtration.

3. Ultrafiltration

3.1 Theory

Ultrafiltration as a process aims to concentrate micromolecular solutions such as protein and polysaccharide solutions as well as cell suspensions. UF, as well as other forms of membrane filtration process, benefit from being energy efficient, often highly selective and compared to many other unit operations, requiring limited space. Other advantages include that they can be performed at modest temperatures, often room temperature, which means that heat sensitive feeds are not negatively affected. This makes UF well suited for the food industry, among other applications. Furthermore, there are no changes of phase or state during UF, which adds to its low energy requirement. However, membranes remain sensitive to fouling for filtering streams containing proteins, starch or pectin. Therefore, when using membranes for food process-related feed streams it is important to investigate fouling and cleaning mechanics [10].

UF is a well-established separation process in the industry. Compared to some other filtration methods, UF is a low-pressure membrane filtration process, typically operating at pressures between 1 to 10 bar. Pore sizes in UF membranes typically range from 0.002 µm to 0.2 µm, resulting in rejections of compounds in the molecular weight range from 1 to 100 kDa. Membrane retention is usually given as molecular weight cut off (MWCO) defined as the lowest molecular weight solute of which 90% is separated in the retentate by the membrane. The driving force for UF is pressure which then filters the solution through the membrane [10].

The objectives for such processes are generally high fluxes, high final concentration and rejection of the solute to be concentrated. It has been well observed during UF processes, that as the concentration of the feed solution increases, the flux will in general decrease, as shown in Figure 1 [2]. However, this is not always the case, as shown by Pritchard et al., who during UF of strongly sheer thinning xanthan gum solution, an increase of flux during the concentration process was observed. It was suggested that this is due to the increase in shear stress at the membrane surface under laminar conditions [11].

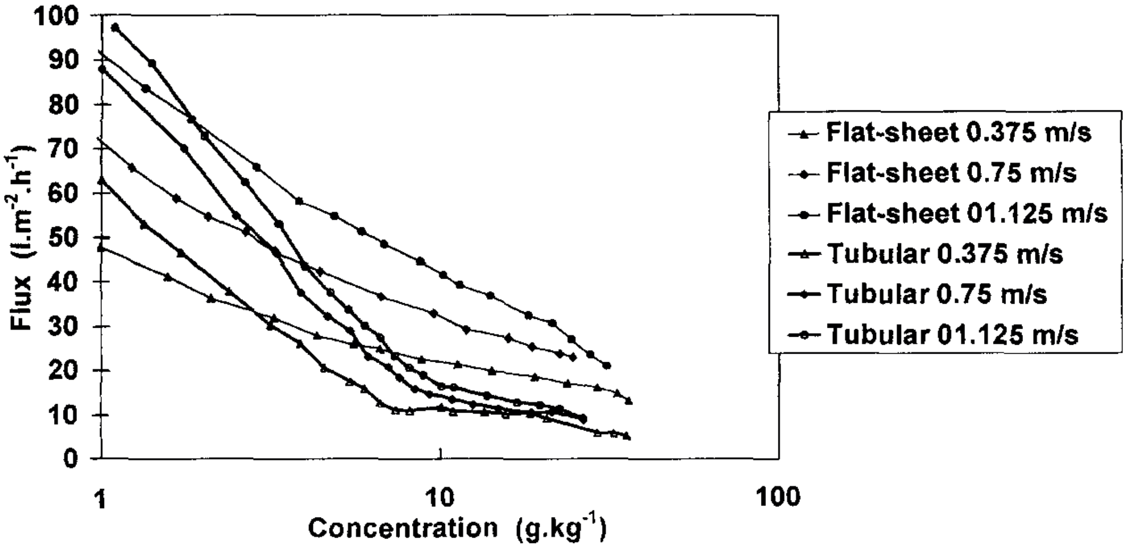


Figure 1. The effect of concentration on the flux of pectin. Figure from Howell et al. [2]

Wang Shu-Sen found that UF flux does not necessarily show linear dependence of the inverse of solution viscosity $1/\mu$, but that this dependency depends of solution viscosity. For lower permeate flux, a small increase in viscosity resulted in a sharp decrease of permeate flux, a liquid with moderate viscosity, a modest decrease was observed when viscosity increased, and for a viscous liquid, the permeate flux was almost unchanged when viscosity was increased, as seen in Figure 2 [12].

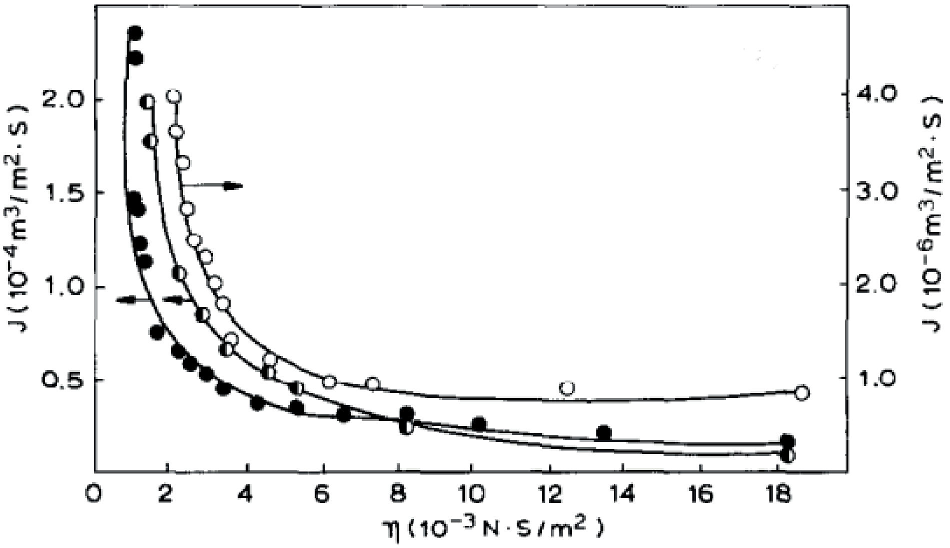


Figure 2. Permeate flux compared to solute viscosity. Glycerine solution, PS membrane (black dots); BSA + glycerine solution, PSA membrane (black and white dots); and polyethylene glycol solution, PS membrane (white dots). Figure from Shu-Sen [12].

A known phenomenon in several transport processes is the existence of a so-called limiting flux, meaning that under certain conditions the transport through the membrane is no longer affected by increasing the driving force. It has been suggested that a viscosity varying with concentration will lead to a limiting flux [13]. Decreasing flux with increasing concentration can sometimes be counteracted by increasing temperature since an increase in temperature results in decreasing viscosity. Increasing pressure across the membrane, known as the transmembrane pressure, has only effect at lower pressures until the limiting flux has been reached. At a higher pressure, the flux eventually stops increasing, reaching a limiting flux, no matter how much further the pressure is increased. However, increasing the crossflow velocity of the feed, or in some other way increasing the mass coefficient away from the membrane, for example by dynamic filtration, can lead to an increase in the limiting flux, which will otherwise decrease at higher concentrations. In practice, possible cross-flow velocity is limited by increasing pressure drop as velocity is increased. To explain and predict these phenomena, mathematical models have been produced analysing the mass transfer close to the membrane surface [11].

A critical parameter for any membrane filtration, as well as almost any other separation process, is that of selectivity. Without a desired selectivity, there is little meaning to the process, no matter how high flux can be achieved. Once an accepted or desired selectivity is reached, then the capacity needs to be considered. The benefits of high fluxes are that they result in less membrane surface area, smaller module sizes and equipment. This reduces the overall costs and is therefore of great interest. Membrane plants, in their nature demanding a combination of mass transport and fluid mechanics to deliver the fluid containing the solutes or suspended matter through the module means that any optimization will affect both the selectivity and capacity. An important consideration in such optimization is the prevention of membrane cake or gel formation, biological film growth, pore plugging and solute intrusion and resultant pore size reduction. Collectively these phenomena are known as membrane fouling [1, 2].

Of special importance for UF in this study, are the following Equations [2, 13].

$$J = \frac{\Delta P}{\mu_p \cdot (R_m + R_f)} \tag{1}$$

$$J = \frac{\Delta P}{\mu_p \cdot R_{tot}} \tag{2}$$

$$R = 1 - \frac{C_p}{C_f} \tag{3}$$

where J is the flux, ΔP the transmembrane pressure, R_m is the hydraulic resistance of a clean membrane, R_f is the resistance of any fouling layer on the surface or within the membrane and R_{tot} is the total filtration resistance. μ_p is the permeate viscosity, C_p is the concentration in the permeate, C_f is the concentration in the feed and R is the retention of the membrane.

UF is classified as a low-pressure membrane process. Major applications for UF include potable water, produced water and products from the biotechnology and food industry [1].

Membrane filtrations has today its given place as a widespread and accepted unit operation within many industries as stated above. The limitations for an even broader application are not the membrane properties themselves but rather mass transfer limitations leading to concentration polarization and fouling [1]. The appearance of a concentration polarization boundary-layer is a natural consequence of the selectivity of a membrane. As permeate passes through the membrane there must be an accumulation of particles or solutes that are retained at the membrane surface. These dissolved molecules reduce the solvent activity, which in turn creates an osmotic pressure and will cause the flow through the membrane to be reduced [14].

Although concentration polarization and fouling may be predictable for clean laboratory feeds using mass transfer models, any feed containing foulants may pose serious difficulty. Since there is no accurate way to theoretically predict the effect of fouling on the flux, a series of experimental tests is often demanded to decide the optimal operating conditions such as crossflow velocity, laminar or turbulent flow, and acceptable wall solute concentration. Usually, the only way to decide optimal process conditions and a good choice of membrane, with the ability to resist fouling, is to extensively screen both process conditions and membrane materials [1].

3.5 Ultrafiltration of molasses

Ultrafiltration of molasses has been covered before in some studies [7, 8, 9, 15 - 19].

Sjölin et al. studied the purification of sucrose using membrane filtration with ceramic tubular 10 kDa MWCO UF and 200 Da MWCO NF. Fluxes of between 20 and 160 l/(h m^2) and low sucrose retention of 0-15% were reported. This experiment however aimed for the sucrose to be collected in the permeate, while macro-molecules were retained in the retentate [7].

In a different study, UF and NF of molasses with the purpose of separating it into its various components for the eventual production of 5-hydroxymethylfurfural were described by Sjölin et al. [15] UF and NF membranes with the same MCWO as in the previous study were used [7]. The enzyme-catalysed hydrolysis reaction is inhibited by various impurities, and thus purification is required. Two different dilutions of molasses were used for each membrane, ranging from a dilution factor of 10 to 200. Results from the UF and NF showed steady permeate fluxes of between 11–34 l/(m^2 h bar) for the NF experiments and 14–27 l/(m^2 h bar) for the UF experiments. Flux recovery was above 80% even after heavy fouling and separation of sucrose approximately in the range of 30-70% for NF and 5-10% for UF [15].

Ryan et al. performed a study involving UF of molasses with the aim of removing macromolecules to benefit ethanol fermentation [8]. A flat sheet membrane module with a polysulfone membrane was used. The membrane used had a MWCO of 300 kDa, however the authors claim that a dynamic secondary membrane consisting of macromolecules develops during operation, reducing the MWCO considerably. The result was substantial reduction of macromolecules but also some unwanted removal of sucrose [8].

A flux study on the separation of sugar from diluted molasses by UF and NF was performed by Mousavi et al. Three membranes were used, UF membranes with MWCO of 10 and 5 kDa and a N30F NF membrane. TMP was varied between 4 and 6 bar, as TMP of 3 bar of less led to a complete stop of flux after some minutes. For the 10 kDa and 5kDa membranes the final fluxes were between 10E-6 to 14E-6 m/s and 6E-6 to 12E-6 m/s respectively, depending on TMP. It was concluded in this study that the UF membranes did not have sufficient rejection of sucrose for a practical application [9].

Luo et al. performed a study using several different NF membranes, each with a MgSO4 rejection of 95% or higher to separate sucrose and reducing sugar in cane molasses as well as a concentration process using a multi-step diafiltration. The result was good separation of sucrose and reducing sugar at 60 °C but insufficient separation at 25 °C [16].

Qing et al. describe how pigments in molasses hinder the use of molasses for fermentation, as the pigments are unable to decompose under this process. The pigments however, are of interest as they act as anti-oxidants and can absorb free radicals. They are therefor of potential value because of possible benefit to human health. A 300 kDa ceramic UF membrane was reported to have been used as a pre-treatment clarification step, followed by adsorption and NF steps. The pigments were retained in the NF retentate [17]. Another clarification study of molasses was performed by Yang et al. Five different UF membranes were compared and membranes with MWCO 30-100 kDa were found to be the most appropriate for these purposes. The threshold flux, defined as the permeate flux where fouling over time sharply increases, was then determined for the different membranes [18].

Guo et al. performed a membrane filtration study involving UF and NF with the aim of decolouration of cane molasses. It was found that NF membranes with a MWCO of 500 D were an appropriate choice for high colour removal and sucrose permeation [19].

3.6 Ultrafiltration of konjac glucomannan

So far there has been limited research performed on the UF of KGM. Earlier studies of on the principles and fouling of KGM using UF have been performed by Aryanti et al [10]. Studies performed using UF systems and membranes having a MWCO of 10 and 20 kDa showed that membranes having larger pore size provide higher flux. Additionally, it has been shown that higher concentration solutions of KGM, give reduced flux. Fouling mechanisms for KGM with a 10 kDa membrane has been described as complete blocking, meaning that the entrance to the membrane pores were completely blocked. This has been strengthened by images of membrane surfaces and cross-sections obtained by scanning electron microscopy. The KGM molecules were shown to both cover the surface and in addition the interpore structure of the membrane was damaged and the membrane, as well as the supporting material were covered by the KGM. For 20 kDa MWCO membrane, the fouling was still severe, however in this case the reason was concluded to be gel layer or cake formation. Higher TMP led to more severe fouling [10].

A study performed by Jian et al. achieved good separation of KGM fragments in different molecular size [20]. This study however involved extensive pre-treatment of KGM using γ-irradiation and the enzyme β-mannanase This highlights the importance of the pre-treatment of the KGM when UF is used. Breaking up the high molecular mass KGM molecules into smaller fragments greatly affects UF performance.

Al-Rudainy performed a study on the separation and purification of hemicellulose (galactoglucomannan), which is similar in structure to KGM, using a variation of separation processes, of which membrane filtration was one part [21]. Best results were obtained using a 50 kDa UF membrane but even then fouling was reported to have been high.

4. Materials and methods

4.1 Raw materials

The performance of two raw materials, molasses and konjac glucomannan (KGM), were studied. Molasses is a low-molar mass material whereas KGM is a high-molar mass material.

4.1.1 Molasses

Sugar beet molasses is produced as a by-product in sugar mills and is considered low value. Traditionally it has been used as animal feed, to sweeten and flavour food and for fermentation purposes. Molasses is rich in the main product of the sugar mill, sucrose, and there is therefore a desire to find more valuable applications. Potentially, sucrose could be separated from molasses and then recirculated back to the main stream of a sugar mill, or it could be used as a raw material in other processes for higher value end products. In this study, molasses obtained from the Örtofta sugar mill, Nordic Sugar AB, outside Lund in Sweden was used.

Various concentrations of molasses solutions were prepared, using 75% total solids (TS) beet molasses and distilled water. However, as the main source of molasses used for this application and context was 81% TS, to be comparable with results from using the 81% TS molasses, all concentrations using the 75% TS molasses were prepared using a slightly higher portion of molasses according to the following concentration factor:

$$Concentration\ factor = \frac{0{,}81}{0{,}75} = 1{,}08 \qquad (4)$$

For example, 10 kg of the 10 wt-% solution was prepared using 1,08 kg of molasses which was then diluted to 10 kg using distilled water.

4.1.2 Konjac glucomannan

KGM is a water soluble, mainly straight chain polysaccharide that is considered a dietary fiber. The origin is Konjac (*Amorphophallus konjac*), a carbohydrate rich plants cultivated in Asia. Uses for KGM include as a food emulsifier and thickener, drug delivery, bio-adhesive improvement, immobilization, encapsulation, film and membrane coating as well as a surfactant it is also marketed as a dietary supplement with claims of relieving constipation and help lowering cholesterol levels as well as reduce body weight [22]. The KGM used in this study was bought as a dietary supplement powder for human consumption (Bulk Powders, Colchester, UK). The quality of KGM is directly dependant on its purity. Methods of separations are thus important. Some methods have involved dialysis or centrifugation, but UF has also been identified as method of promise [10].

To decide an appropriate viscosity for the first attempt, solutions of three different concentrations were prepared of 0,1, 0,5 and 1 g/l of KGM in approximately 200 ml of distilled water. The samples were then put in a water bath of 80 °C for approximately 20 hours. This was done to cause some partial hydrolysis of the KGM molecules. The viscosity was then measured for each solution at 50 °C and the results are presented in Figure 3 with water at 50

°C included as a reference value. From these results, it was decided that the 0,5 g/l with a viscosity of about 1 mPa*s would be a good concentration for a first attempt. Further concentrations for KGM experiments were then chosen to match the viscosity of molasses experiments.

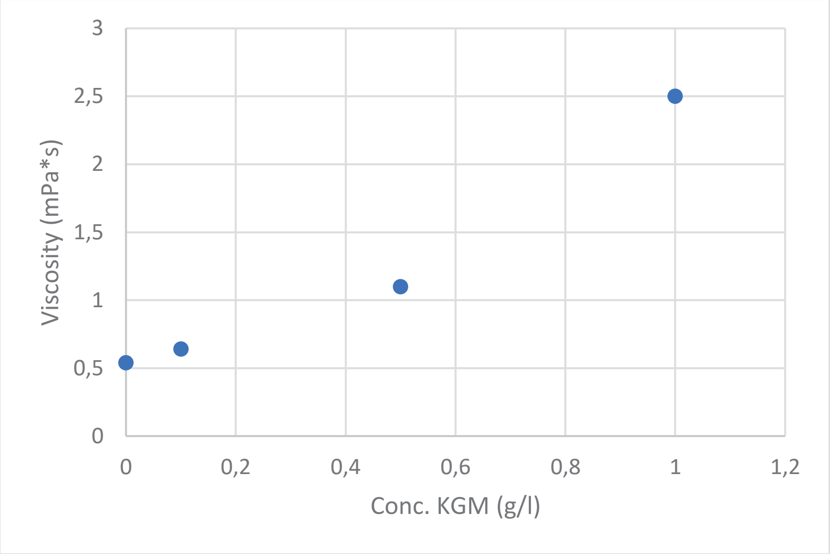


Figure 3. Viscosity test for various concentrations of KGM at 50 °C, with pure water included.

4.2 Membranes and equipment

4.2.1 Membranes

The Alfa Laval RC70PP membrane (Alfa Laval, Nakskov, Denmark) was used for these experiments. The RC70PP is a polymeric membrane made of regenerated cellulose acetate on a polypropylene backing with a MWCO of 10 kDa [23]. The membranes were placed with plastic clips on the support plates, which were then placed together and compressed with bolts. The membranes being installed in the Alfa Laval M39 membrane module can be seen in Figure 5.

Figure 5. RC70PP membrane *installed in the M39 module.*

The membranes were washed with Ultrasil 110 (Ecolab, Älvsjö, Sweden) and thoroughly rinsed with de-ionized water as instructed by the manufacturer. The pure water flux (PWF) was then measured. This was done by setting three different pressures, approximately 0,5 bar apart at a flow of 4 m^3/h at 30 °C, and measuring the flux for 5 minutes at each pressure. Each flux was then divided by its corresponding pressure, and the average flux of these three fluxes was calculated to arrive at a value denoted as the permeability (J_p) with the unit $l/(m^2\ h\ bar)$.

$$J_p = \frac{1}{3}\left(\frac{J_1}{P_1} + \frac{J_2}{P_2} + \frac{J_3}{P_3}\right) \qquad (5)$$

Between the KGM experiments, alternating washes of the membranes were done using Ultrasil 110 and Ultrasil 73 (Ecolab, Älvsjö, Sweden).

4.2.2 Equipment

The Alfa Laval LabStak M39 (Alfa Laval, Nakskov, Denmark) module was used in the experiments. This is a plate-and-frame crossflow membrane filtration module, in which up to 5 plates, each supporting 2 membranes, are fixed. The membranes were placed with plastic clips on the support plates, which were then placed together and compressed under a metal plate with bolts. The assembled M39 is shown in Figure 6. In these experiments, the membrane module contained three support plates and six membranes, as a membrane is attached to either side of the plate. The M39 plates have a rectangular shape with rounded ends. While the unit can be installed for either parallel flow or counter flow, this particular unit had already been set up for parallel flow. Each membrane support plate is composed of a perforated surface and an inside cavity through which the permeate passes. A schematic illustration of the module can be seen in Figure 7 and a cross section illustration in Figure 8.

Each plate module of the M39 unit consists of 10 channels, separated by interior walls. Each channel has the height of 2 mm and a width of 16 mm. The length of each channel is the total length of the membrane which is 0,55 m. Each membrane has the area of 0.1 m^2, and with each plate holding two membranes and 3 as plates were used, the total membrane area of the M39 unit in this set up was 0.6 m^2.

Figure 6. Labstak M39 equipment.

The M39 module was part of an Alfa Laval Combi M39/3.8 pilot unit (Alfa Laval, Nakskov, Denmark) with an auto-regulated pump for easy flow selection, an open access feed tank and a pressure valve to set the desired pressure as well as a pressure gauge. A heat exchanger and a thermometer were also attached. To supply cooling, a simple solution was provided by attaching a water hose to cool the pipe surface. The unit works according to crossflow principles, the flow enters the unit at one end, the permeate flow through the membrane, into the plate and exits at the end of the unit separately from each plate. It can either be collected or recirculated into the feed tank. The retentate exits the unit at the same side as the permeate and can likewise either be recirculated or collected.

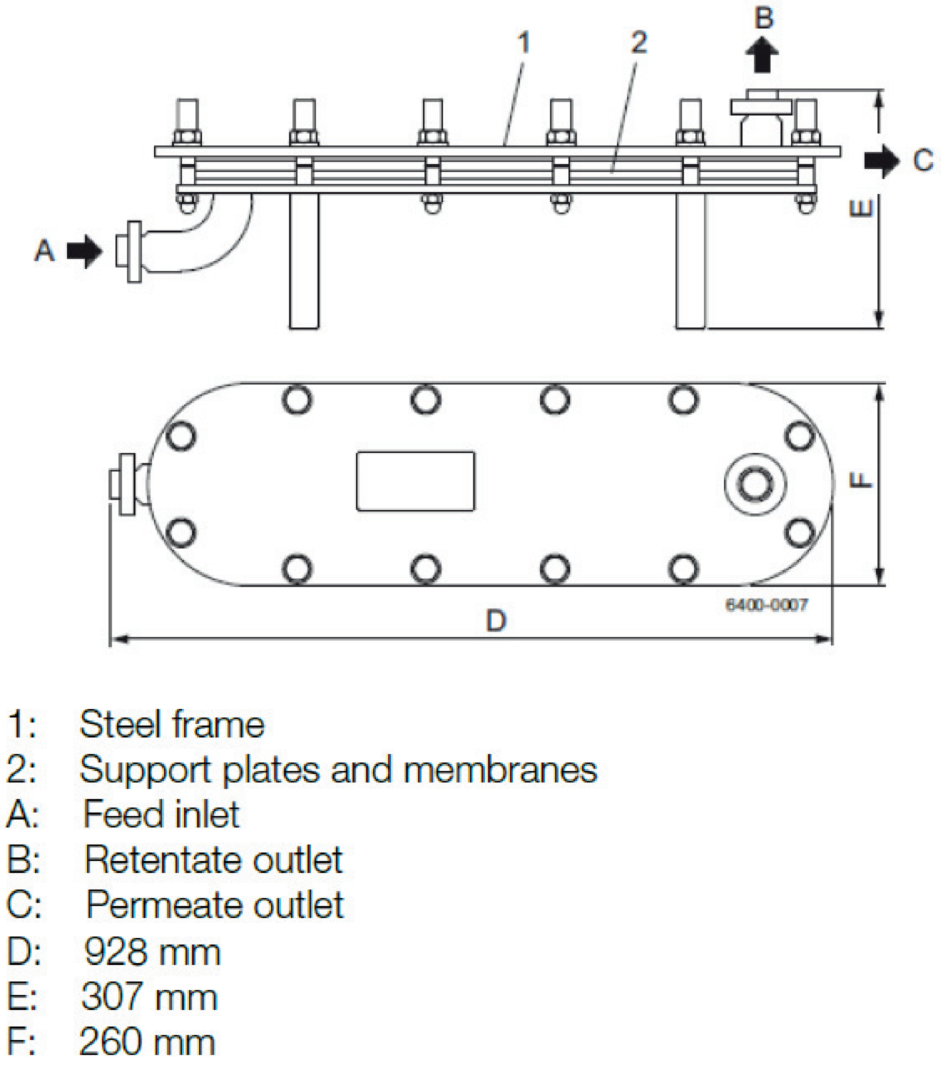


Figure 7. Schematic illustration of the M39. Figure from Alfa Laval [24].

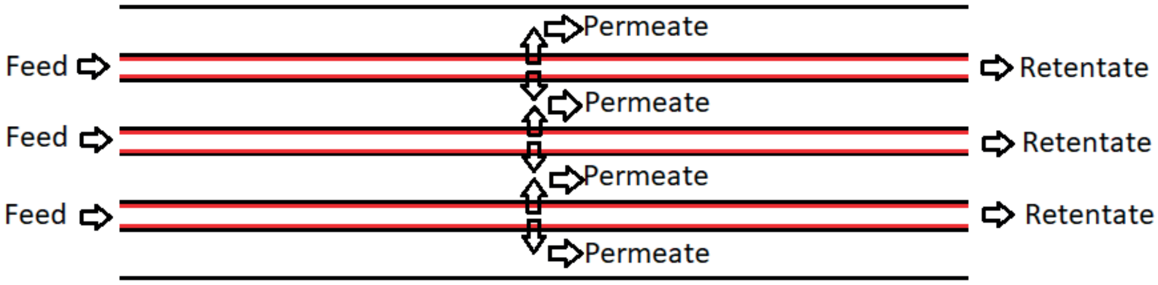


Figure 8. Illustration of a cross-section of the M39. Feed flows through channels from left to right, permeate flows through membranes highlighted in red, enters permeate cavities in the plates.

4.3 Experimental procedure

4.3.1 Flux experiments

It was decided that all experiments would be made using the same parameters to achieve comparable results. A flow of 4 m^3/h, corresponding to a velocity in each feed flow channel of 0.86 m/s, was chosen since this was close to the maximum of what the M39 unit could reliably perform, without causing too large operational flow variations. Initially, the flow was desired to be higher to be well within turbulent flow, however certain practical limitations as well as the high viscosity of higher concentrated molasses solutions meant that a compromise had to be made and by calculating the Reynolds number for the different concentrations a flow pattern more in the border land between turbulent and laminar flow for lower concentration and fully laminar for higher concentration was estimated, which was seen as acceptable.

The transmembrane pressure was decided to be 3 bar, as this was considered enough to generate a steady flux and permeate but well below the maximum value of 7 bar specified by Alfa Laval for the M39 module. The temperature was decided to be 50 °C because this was expected to give good solubility of the molasses.

First the membranes were cleaned. This was done using the alkaline detergent Ultrasil 110. A 0.5 volume-% mixture was prepared and recirculated through the module for 1 hour at 40 °C at slightly above 1 bar transmembrane pressure.

At each experiment, approximately 15 kg of solution was prepared. This was done by diluting pure molasses to the correct concentration with distilled water and heating the volume to 50 °C while stirring. The M39 module was then heated to 50 °C, after which the distilled water present in the unit was drained to almost the point of the pump sucking air when the molasses solution was swiftly added. The retentate was then discarded until it changed from a transparent to a distinct brown colour to remove as much of the dead volume water as possible. The retentate was then recirculated into the feed tank. However, as water at these flow rates forms far from a perfect plug flow, some dilution of the feed from the already present water was unavoidable. Since the actual concentration would therefore be different from the calculated concentration of the added molasses solution due to the diluting effect of the dead volume, the

Brix of the solution was measured immediately after the retentate started being recirculated to the feed tank. This was done to know the actual concentration. The Brix for the permeate was also measured. At the very end of each experiment, the Brix of both the feed and permeate were measured again.

The feed was then recirculated at 3 bar transmembrane pressure and a flow rate of 4 m^3/h during which the permeate flux was automatically monitored and logged. The recirculation was performed for a total of 4 hours. Of special interest was the last 1 hour, when a steady state performance was considered to be established.

The KGM solutions to be used in the M39 module was prepared by mixing a 25-litre solution KGM powder and 50 °C distilled water. This solution was then heated for 24 hours at 80 °C in a tank with continuous stirring, as seen in Figure 9, the apparatus taking about 4 hours before the target temperature was reached. Thereafter the solution was put aside to cool to 50 °C, while sporadically stirred. When at 50 °C the whole 25 l solution was swiftly added to the M39 feed tank, while as much as possible of the dead volume water retentate was discarded.

The experiments with KGM were performed using the same operation parameters as in the experiments with molasses. A flow of 4 m^3/h, at 50 °C and 3 bar TMP for 4 hours were used.

Figure 9. Stirred heated tank for 24 hours KGM preparation.

The permeate flux was measured by an automatic flux meter and logged continuously on a computer. Although the total membrane area was 0.6 m^2, for calculation purposes the effective membrane area was estimated to 0.5 m^2. This was done since the outer plates of the M39 underperform and the top and bottom membranes were therefore estimated to perform only at 50% efficiency.

It was discovered mid-experiment that the flux meter registered low fluxes (below 10 l/(h m^2)) as zero. When further investigated the flux meter was revealed to also register intermediate fluxes (10-50 l/(h m^2)) as too low, but worked well for higher fluxes (above 50 l/(h m^2)). Hence all intermediate fluxes had to be recalculated using a calibration curve, as the logged values were not perceived to be accurate. This calibration curve was made during the second 30% molasses experiment but considered applicable for all concentrations. The flux curve was again validated for the KGM experiments. The calibrations curve and resulting mathematical expression are shown in Figure 9. Fluxes in the proximity of 10 l/(h m^2) or less were measured by hand using a timer and a measuring cup.

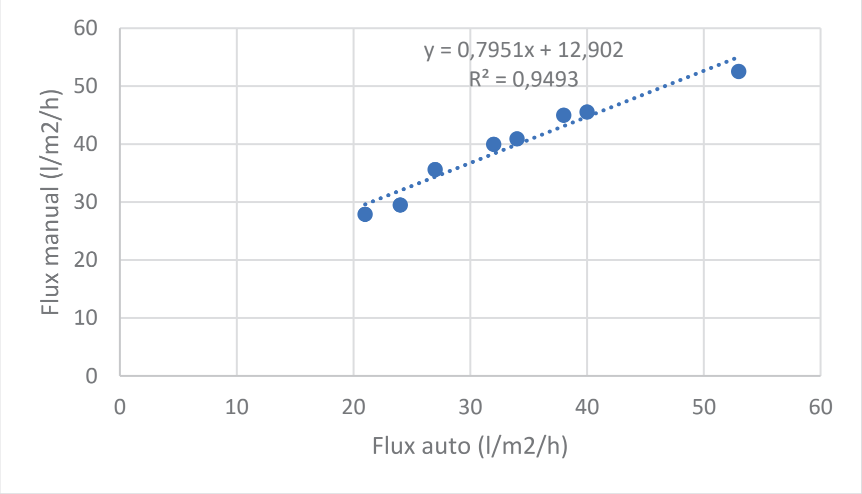


Figure 9. Calibration curve made during 30% molasses experiment.

4.3.2 Membrane cleaning and pure water flux

After the filtration of each molasses concentration was completed, the PWF was measured as described above. The membranes were then cleaned by recirculating a 0.5 volume-% Ultrasil 110 solution for 1 hour at 40 °C with a membrane pressure of about 1 bar. Then the PWF was measured again for comparison.

After each KGM experiment, multiple cleanings had to be done. As alkaline Ultrasil 110 proved insufficient, acidic Ultrasil 73 was also used. Since a 0.5% solution of U73 had a pH low enough to damage the membranes, pH was adjusted by using a combination of approximately 70% U73 and 30% U110 in the same cleaning for a total of 1 volume-%

detergent. In this way, pH was managed to be around 3, which was considered a good compromise between cleaning effect and taking care not to damage the membranes. Repeated cleanings of a combination of U73 and U110, as well as cleanings using only U110, were done. Before and after each cleaning, the PWF was measured in the same way as for the molasses experiments. Between cleanings, the M39 was usually left overnight at a slow but steady flow of around 1 m^3/h and 1-2 bar transmembrane pressure to thoroughly rinse the membranes.

4.4 Analysis

4.4.1 Viscosity Apparatus

For viscosity measurements the Modular Compact Rheometer MCR 302 (Anton Paar, Graz, Austria) shown in Figure 10, was used. The MCR measures viscosity at set shear rate points and gives a viscosity at each value. As can be seen in Figure 11 the viscosity will be different at each shear rate measurement point for a pseudo-plastic liquid, and approximately the same for a Newtonian one. In this study, most liquids showed a Newtonian behaviour, including all molasses samples. In this case, for a final viscosity value, a few points at the highest shear rates were chosen, outliers were removed, and an average was calculated. For pseudo-plastic liquids (a few KGM feeds only) viscosity was taken at a shear rate of 50 s^{-1}. Two result charts of the viscosity determinations are shown in Figure 11.

Figure 10. MCR 302

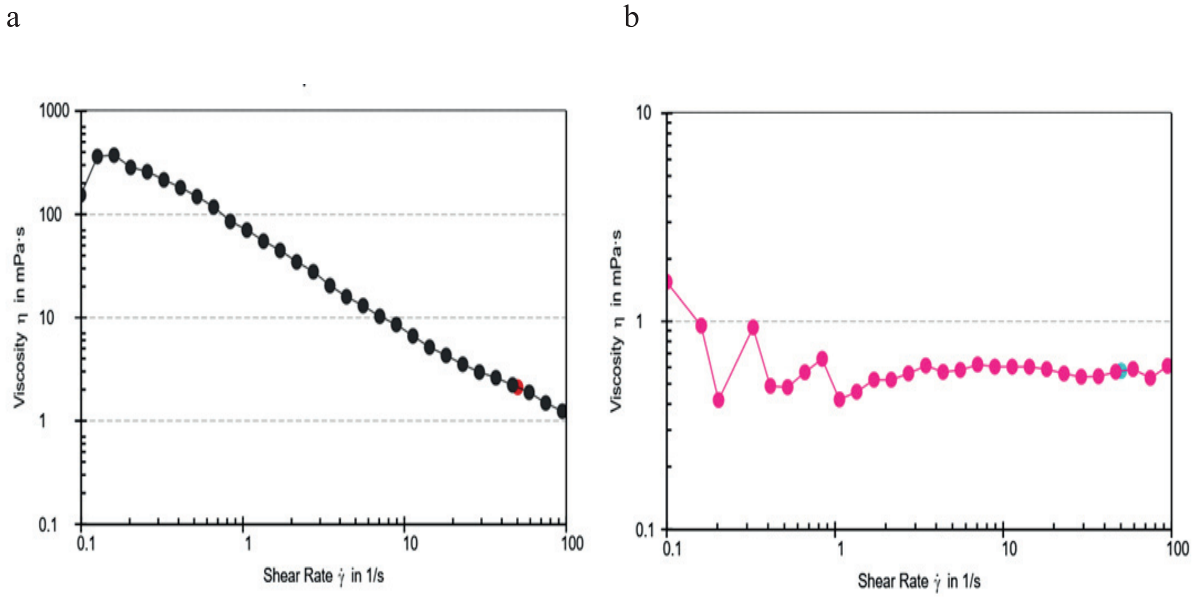


Figure 11. Non-Newtonian viscosity chart of 0,3 g/l KGM feed (a) and Newtonian 0,3 g/l KGM permeate (b).

4.4.2 Brix

The concentration of molasses was determined by measuring the brix of the sample. Brix was measured using a portable refractometer (Hanna instruments, Woonsocket, USA). The sensor was cleaned with distilled water, zeroed, and then a small sample of solution was applied, after which the Brix was measured and recorded.

4.4.3 Total dry solids

The concentration of the KGM was determined as total solids content. 10 ml samples were poured into aluminium forms as shown in Figure 12, weighed, dried for 24 hours at 110 °C and weighed again. Note the long fibrous hair like appearance of the dried KGM substance.

Figure 12. Dried sample of KGM.

Retention was calculated from dry weight measurements. Samples from feed and permeate at the start and end of each experiment were collected, for a total of 4 samples for each KGM concentration.

5. Results

The performance of two viscous solutions during UF with the RC70PP membrane were studied. Molasses contains low-molar mass components and has low viscosity and Brix retention, while KGM has high-molar mass molecules and high retention for viscosity and TS. The influence of viscosity on flux was investigated and compared for the two different feeds.

5.1 Viscosity determination

The influence of the concentration of molasses on the viscosity was studied at 10, 40, 50, 60, 70 and 80 wt-% of molasses. Duplicate measurements of viscosity for each concentration were done and are shown below in Figure 13. Two exponential trendlines were adapted in excel, the intersect of the two lines was calculated to be at the concentration 52,2%. This point and the surrounding region were seen to be of great interest for the UF experiments because of the steeper increase of the viscosity, and therefore a more pronounced flux decrease was expected.

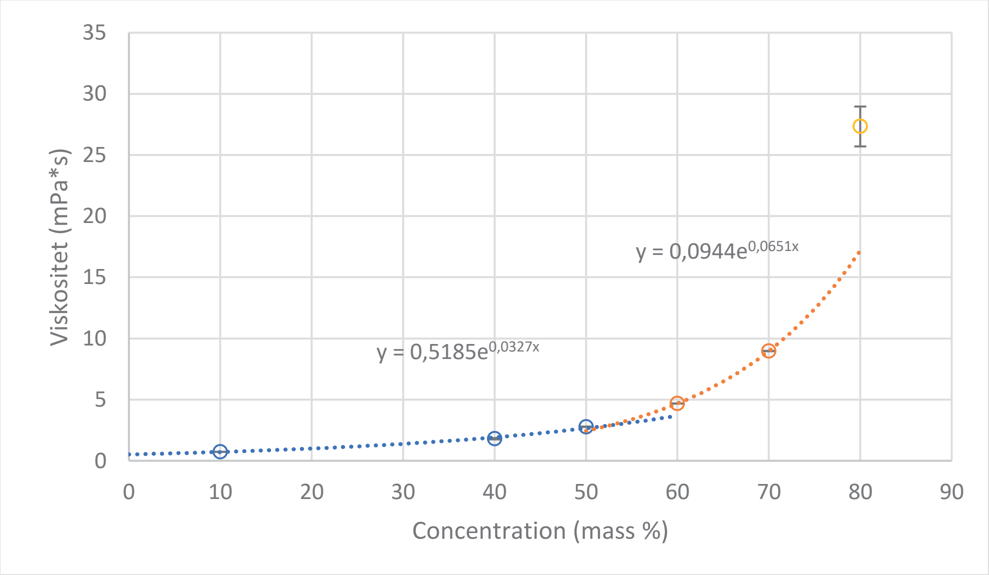


Figure 13. Viscosity for various wt-% of molasses at 50 °C.

5.2 Experiments with molasses

Solutions of 10, 15, 20, 30, 40 and 50% molasses were prepared the day the respective filtration was made. Initially it was planned to do 60, 70 and 80% as well, however at 50% the flux was considered so low that the study of further concentrations was considered to have little value.

5.2.1 Flux of molasses

Each experiment lasted 4 hours. With the automatic flux meter, the flux was measured every 10 seconds, and was plotted with a 1 minute moving average. The manual measurements were done as often as practical and care was taken to make as many measurements as possible especially at the beginning of each experiment, when flux was expected to change most. The flux was almost constant throughout the experiment at the lowest concentration (10%), whereas it decreased over time with at all other concentrations. It is likely that the decrease over time seen in all other cases was caused by molasses molecules that adhered to the membrane surface over time and prevented the permeate to pass through. In the 10% case, it can be speculated that the concentration of such molecules was not high enough to cause the flux to decrease. The fluxes during the experiment at the lowest, 10% and highest concentration, 50%, of molasses are shown in Figure 14.

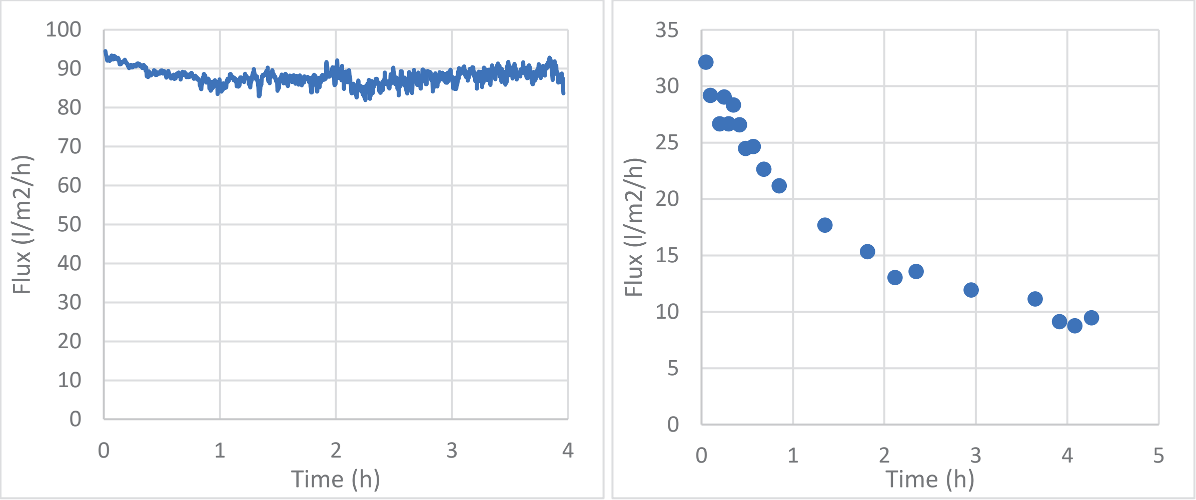
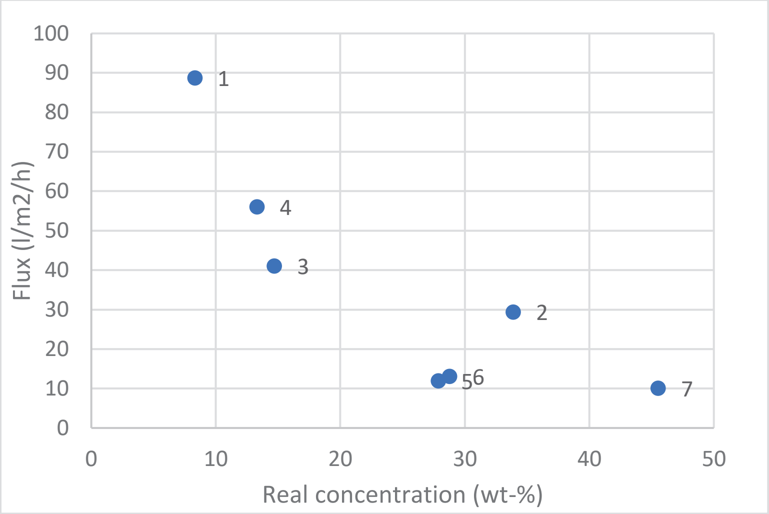


Figure 14. Flux during the experiment at 10% molasses using the automatic flow meter (left) and 50% molasses with manual measuring (right).

The flux decreased with increasing concentration and increasing viscosity, as shown in Figure 15. The flux values at 30% (5 and 6) are assumed to be outliers even though duplicate measurements gave almost the same result. Possibly, the 40% (2) experiment could instead be the outlier. Specific values of flux, Brix and viscosity can be found in Appendix A. As can be seen in Figure 15, a clear correlation between flux and concentration could be observed. This result is well in line with results of other studies, as shown by Howell et al. [2] and Pritchard et al. [3]. Fluxes in these experiments were generally within the same range as reported in other similar studies, including 30-120 l/(h m^2) at 3 bar TMP [7], 40 l/(h m^2) [18] and 17 l/(h m^2) [19].



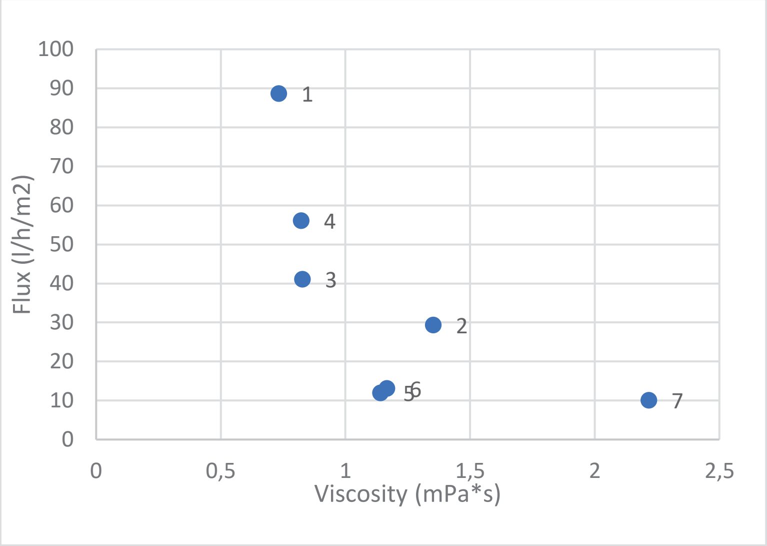


Figure 15. Flux compared to real concentration (top) and feed viscosity (top) after 4 hours for all experiments. The number is the chronological order of the experiments.

The order of the concentrations for the experiments were 10, 40, 20, 15, 30, a repeat at 30, and 50%. This was done as the reduction in flux from 10 to 40% was greater than expected, and a clearer understanding of the flux reduction as an effect of concentration between 10 and 40% was needed. The membranes were rinsed with deionized water after each experiment and the PWF was measured. The membranes were then cleaned and PWF was measured after cleaning. After some experiments (15%, 2nd 30% and 50%) several, subsequent cleanings were performed in order to investigate if it would be possible to recover the initial PWF of the membranes. Fluxes and PWFs in chronological order throughout the experimental series are shown in Figure 16.

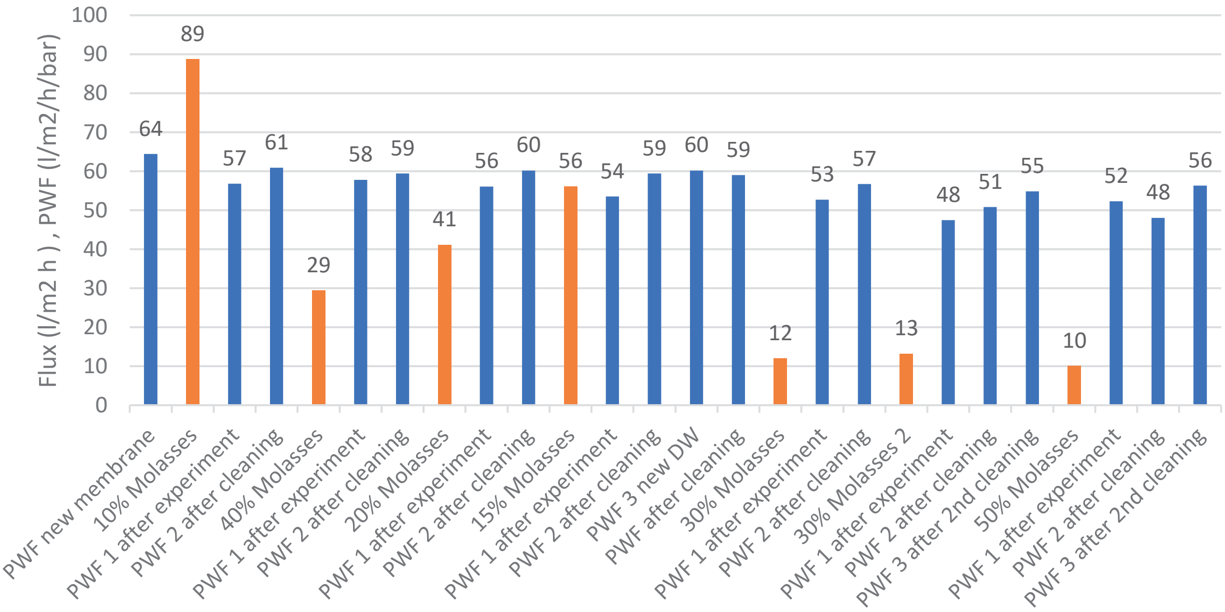


Figure 16. All experiments in chronological order. Note that the molasses experiments were done at the pressure of 3 bar, while the PWFs are presented in the unit /bar. Orange staples denotes flux of molasses solutions and blue staples denotes PWFs.

5.2.2 Retention of molasses

Real concentration (Real C) was not the same as the prepared concentration. The reason was the dilution of the prepared solution which happened when it was added to the M39 module, as there was always a dead volume of water present since the module could not be completely drained. Real concentration was calculated according to Equation 6:

$$Real\ C = \frac{Brix\ sample}{Brix\ pure\ molasses} \tag{6}$$

Brix for all samples and pure molasses can be seen in Table 4, Appendix C.

Presented below is the Brix in Table 1, and the viscosity in Table 2, for the feed and permeate at the start and at the end of the experiments for 10% and 50% molasses. These two concentrations are presented because they represent the lowest and the highest used concentration and represent the most outlying results. It can be observed that flux greatly decreased from the lowest to highest concentration, and that retention was very low for the lowest concentration and only increased slightly at the highest concentration. Values for all experiments can be seen in Table 4, Appendix C.

Table 1. Concentration, flux and Brix of feed (F) and permeate (P) at the beginning of the experiment (0h) and at the end (4h).

Conc	Real C	Flux (l/m^2 h)	Brix			
			F-0h	F-4h	P-0h	P-4h
10%	8%	88.7	6.5	6.6	6.3	6.4
50%	46%	10.1	35.6	37.0	34.8	36.4

Table 2. Concentration, flux and viscosity of feed (F) and permeate (P) at the beginning of the experiment (0h) and at the end (4h).

Conc	Real C	Flux (l/m^2 h)	Viscosity (mPa*s)			
			F-0h	F-4h	P-0h	P-4h
10%	8%	88.7	0.86	0.73	0.71	0.71
50%	46%	10.1	2.03	2.22	1.88	2.03

Real concentrations were calculated according to Equation (6). The retention of molasses, calculated according to Equation (3) was on average 5.2% based on viscosity and 3.5% based on Brix, during the experiments. No clear dependence on the concentration for Brix retention was observed, as shown in Figures 17. The retention for viscosity was sometimes so low that there was little difference between permeate and feed, which can be seen for the viscosity retention for the 15% real concentration, as seen in Figure 18 and also in Table 4, Appendix C. The low retention for Brix, is somewhat in line with earlier studies of the UF of molasses which has been in the region of 5-10% [15], approximately 12%. [19] or approximately 2-8% [18]. Considerably higher retention has been reported in literature for other types of membrane filtration, such as NF, including 90% [19] or almost 100% for some NF membranes [16]. For viscosity retention, a weak linear trend could possibly be observed as can be seen in Figure 18.

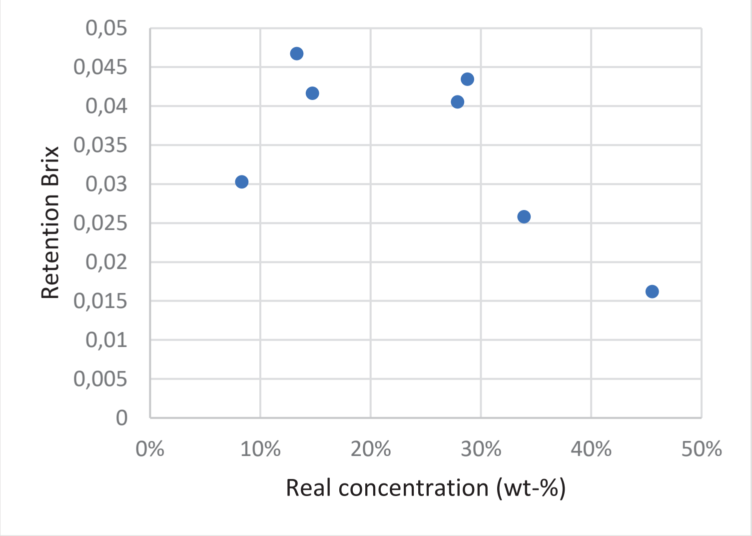


Figure 17. Retention based on Brix in the feed solution at 4 h.

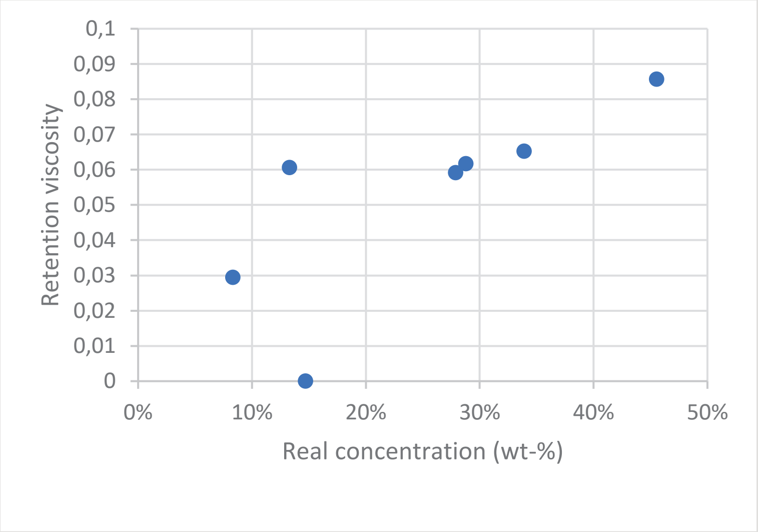


Figure 18. Retention based on viscosity data in the feed solution at 4 h.

5.3 Experiments with konjac glucomannan

The KGM experiments were performed under the same experimental conditions as in the molasses experiments. In Figure 19 the typical appearance of a KGM flux curve is shown. Remaining KGM flux curves can been seen in Appendix B. It can be observed that compared to molasses the KGM flux curve fluctuated considerably more but much sooner reached a stable average flux over time. The initial drop in flux was also much more rapid, suggesting that fouling happened quickly, but then no significantly increased over time. This is well in line with other studies, as presented for example by Aryanti et al. [10] showing the same rapid decrease in flux, as well as a clear correlation between increasing concentration and decreasing flux

As with molasses, the flux curve was recalculated using the calibration curve in Figure 9. Results were validated by also measuring the flux manually as shown in Figure 19, demonstrating that the calibration curve was applicable and accurate for KGM as well.

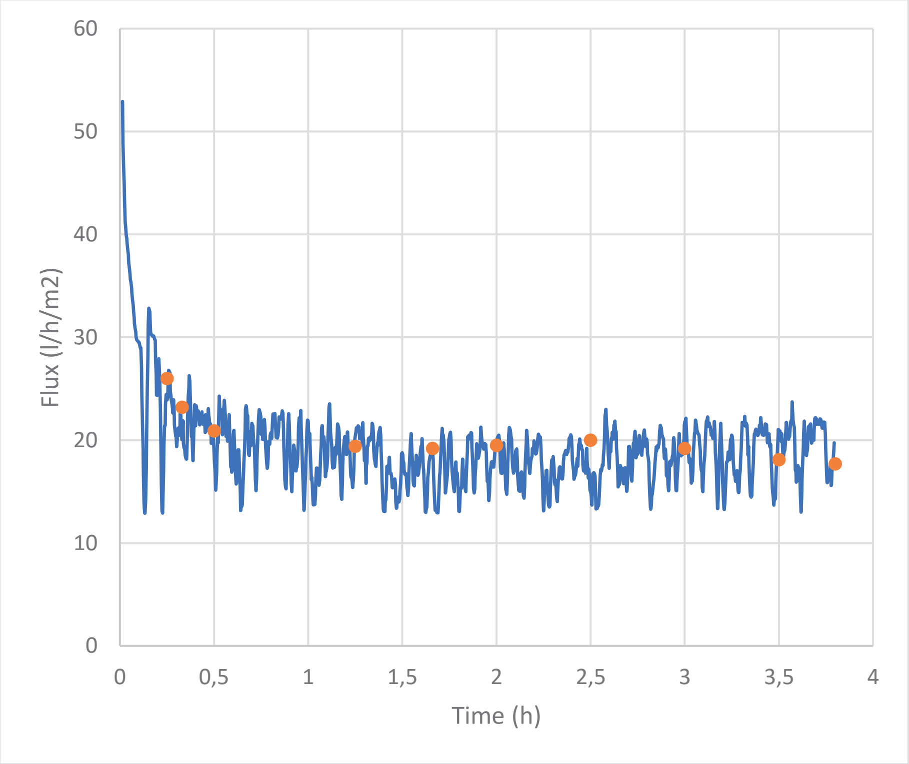


Figure 19. Flux curve for KGM 0,85 g/l with automatic measurer (blue line) and manual measurements (orange dots). Last hour average 19,1 and 18,8 respectively.

As with the molasses, a reduction in flux as the viscosity increased could be observed. This is shown in Figure 20. The reduction rate in flux was quite similar compared to the same viscosity range for molasses. Further experiments would be required to investigate how the flux behaves differently than for the molasses experiments for viscosities outside this range.

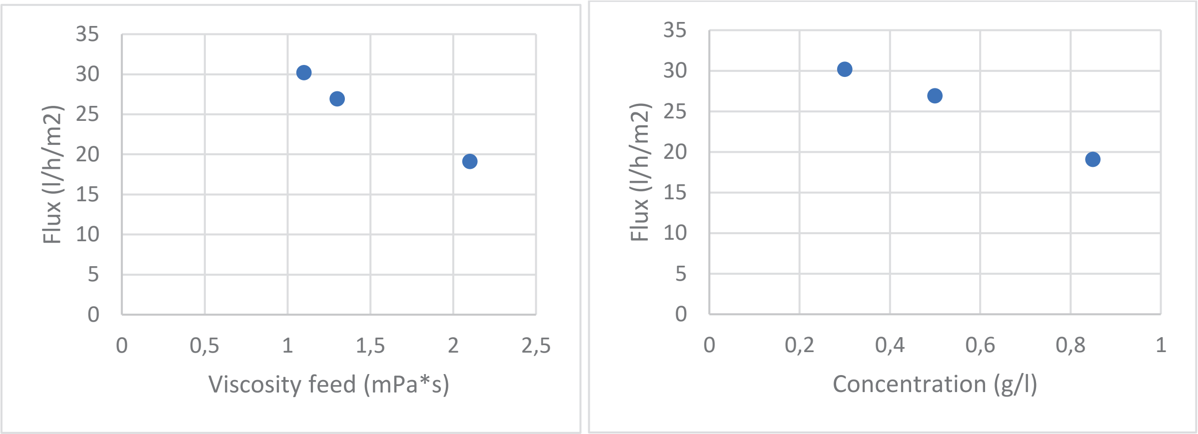


Figure 20. Flux for KGM shown for the viscosity of the feed (left) and concentration (right).

Shown in Figure 21 is the result of all KGM experiments as well as all PWF in chronological order. For the KGM experiments, fouling was a real concern. The considerable problems considering cleaning can be seen in that the PWF which very sharply decreased after each experiment and was not recovered. This problem accumulated for each experiment and from Figure 21 it is likely that permeate flux of further experiments would be eventually hindered due to fouling, or other detergents would have to considered. This difficulty with fouling when long polysaccharides are concerned has been previously described by Aryanti et al. [10] using KGM and Al-Rudainy using galactoglucomannan [21].

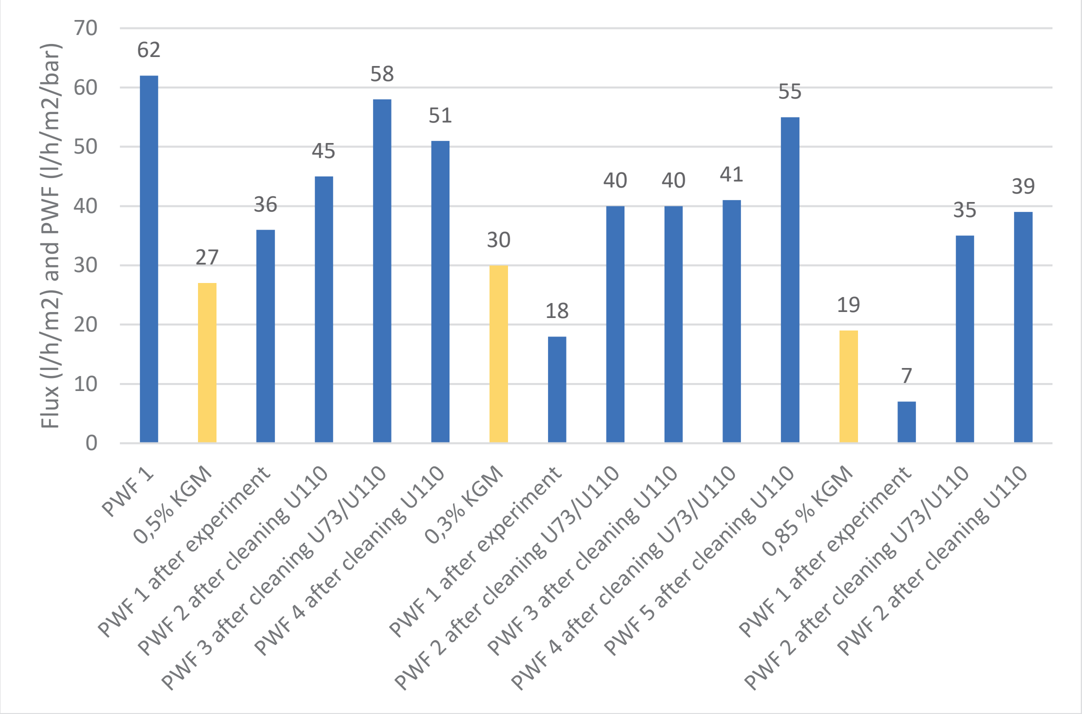


Figure 21. Last hour average flux for all KGM experiments and PWFs.

5.3.1 Retention of konjac glucomannan

Retention of KGM was calculated according to Equation (7) using TS as concentration and the results presented in Table 5 in Appendix D. Since three results were almost the same and one result was somewhat close, it was concluded that the retention was approximately 80%. Stronger results for the dry matter determination could have been obtained if a larger amount of liquid, preferably several dl, would have been used.

$$R = 1 - \frac{TS\ Permeate}{TS\ Feed} \tag{7}$$

It was observed that the permeate viscosity has little effect on flux for the KGM experiments. According to Equation (2) R_{tot} was plotted for each feed concentration. A strong correlation between R_{tot} and the feed viscosity was observed as seen in Figure 22. This suggests, as discussed above, that fouling increased with concentration and viscosity as more KGM molecules attached to the membrane and prevented permeate from passing through the membrane.

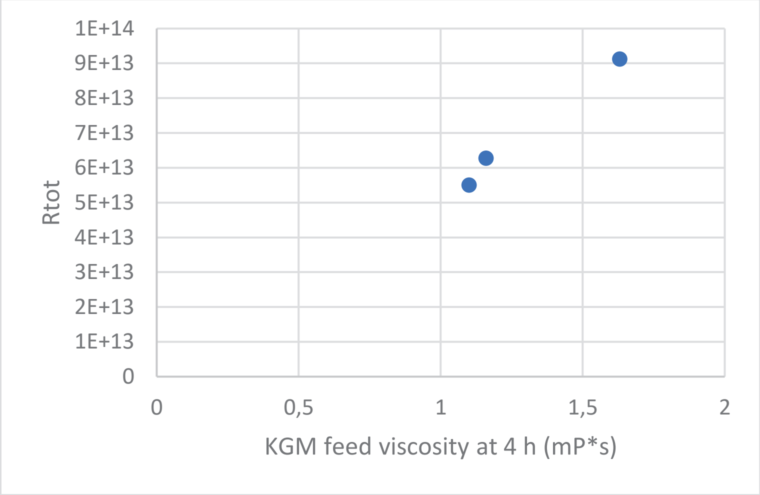


Figure 22. Rtot for all the feed viscosity at 4 h for all KGM experiments.

6. Modelling

6.1 Model

Part of this study aims to use experimental results and data to create a model which could be used to predict results when changing operational parameters. This part of the study was limited to simulations of molasses as feed solution. Since the experimental part of this study was to a large degree an examination of the effect of viscosity on membrane filtration, this model mainly focused on modelling of flux by varying viscosity through changing temperature and concentration. To be relevant, values obtained from experimental results were analysed and used. The simulations in this study were done using Comsol Multiphysics, Comsol AB, Stockholm, Sweden.

Three studies were performed. The aim of the first simulation was to show the change of the concentration and viscosity during membrane filtration, at same or similar conditions as in the actual experiments. A cross-section of a single plate of the M39 module was used when modelling the concentration profile, with the boundary at the top and bottom representing the membranes as shown in Figure 8.

A time dependent study was done in the second study where a 50 l starting volume was filtrated through a membrane with 95% retention of molasses. The reason for using a retention of 95%, instead of the actual experimentally determined retention of 5,2%, was that this was seen as a more realistic retention for an actual membrane process and therefore of greater interest to model. Likely a membrane with lower MWCO than typically used in UF, meaning NF or reverse osmosis, would be required. Similar retentions have been achieved by Luo et al. using NF [16]. The permeate was continuously removed while the retentate was recirculated to the feed tank. A schematic illustration of this process is shown in Figure 23. The simulation was run for a total time of 2 hours.

In the third study, the permeate flux was simulated under the same circumstances as during the experiments, but temperature and feed concentration were varied.

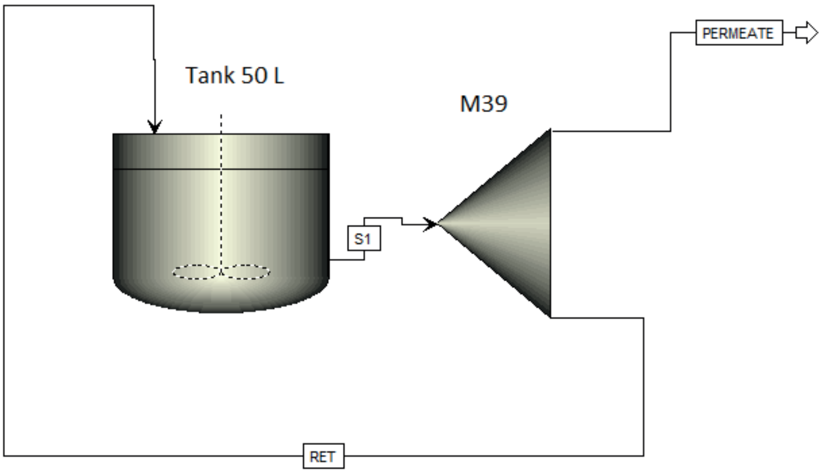


Figure 23. Schematic illustration of time dependent study.

The following equations were used to calculate concentrations and velocities in Comsol [25].

$$Re = \frac{v \cdot D_h \cdot \rho}{\mu} \tag{8}$$

$$\rho \frac{\partial v}{\partial t} = -\rho v \nabla \cdot v + \mu \nabla \cdot v - \nabla \rho \tag{9}$$

$$\frac{\partial c}{\partial t} = -v \cdot \nabla c + D \nabla \cdot \nabla c \tag{10}$$

The following equations were used to calculate the flux and the concentration in the recirculated retentate.

$$J = \frac{\Delta P}{\mu_f \cdot V_f \cdot R_{tot}} \tag{11}$$

$$C_{in}(t) = \frac{m_0 - \int m(t)\, dt}{V_0 - \int V(t)\, dt} \tag{12}$$

Equation (11) is the same as Equation (2) but the viscosity of the permeate, μ_p, has been replaced with the viscosity of the feed, μ_f, multiplied with an experimentally determined factor denoted as the viscosity retention factor (V_f), calculated according to Equation (13).

$$V_f = \frac{\mu_p}{\mu_f} \tag{13}$$

Calculated V_f values are shown in Figure 24. Since there did not appear to be any strong relationship between V_f and Brix, and since the values do not differ very much, an average value for V_f of 0.95 was used in the calculations in Comsol.

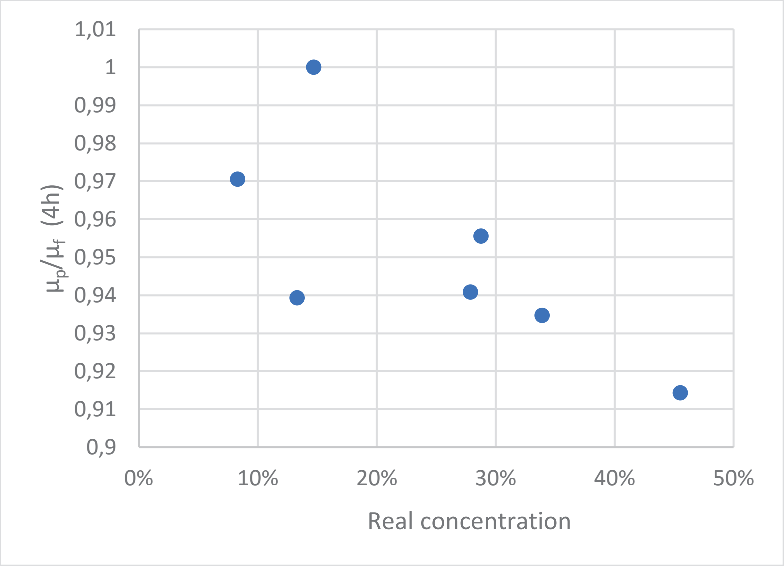


Figure 24. Permeate viscosity divided by feed viscosity after 4 hours for all experiments.

The initial mass of molasses was set as 5 kg giving an initial concentration of 0,1 kg/l or 10 wt-%. Other constant values used in the simulations are found in Table 3, where l is the membrane length, h is feed channel height, A is total membrane area, P is trans membrane pressure, R is membrane retention, V_0 is starting volume, C_0 is starting concentration, v_0 is feed inlet velocity, M_0 is the initial mass of 100% molasses and V_f is viscosity retention factor.

Table 3. Parameter list for comsol simulation.

L	0.55 m	V_0	50 l
h	0.002 m	C_0	0,1 kg/l
A	0.50 m²	v_0	0,86 m/s
P	3E5 Pa	M_0	5 kg
R	0.95	V_f	0,95

Equation (2) was used to calculate the R_{tot} value, the total hydraulic filtration resistance, for each experiment. The last hour average flux during the experiments was used in the calculations. R_{tot} values at different concentration and viscosity are shown in Figure 25. No clear pattern for R_{tot} could be immediately observed. However, by removing the outliers at 30%, marked in orange, and using linear regression on remaining values, a linear expression was obtained which gave R_{tot} as a linear function of feed viscosity as shown in Equation (14).

$$R_{tot} = 2.22E16 \cdot \mu_f + 6.23E12 \tag{14}$$

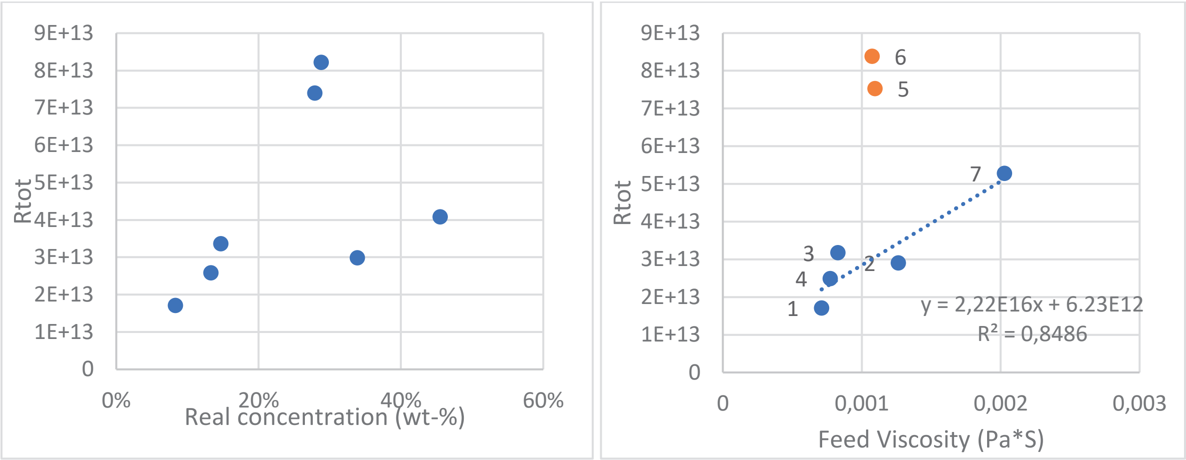


Figure 25. R_{tot} for all experiments plotted against real concentration (left) and feed viscosity, with removed outliers in orange and linear expression for R_{tot} (right).

The permeate flux was given according to Equation (11), using the R_{tot} value as calculated from Equation (14). The concentration of molasses in the recirculated retentate, C_{in} (wt-%), was calculated using Equation (12) in which the total amount of molasses and volume removed from the system with the permeate at any given time are subtracted from the starting amount of molasses, M_0, and the total volume, V_0. m(t) is the amount of 100% molasses which is removed at any time (t) with the permeate and V(t) is the volume which is removed at any time as permeate. As the Reynolds number, calculated with Equation (8) was well below 2000 for all concentrations, the Comsol simulation was done using a laminar flow model.

Three different values for R_{tot} were used to calculate fluxes corresponding to the same concentrations as used in the experiments. For R_{tot}, first a simple average for all experimental values was calculated, and then another average was calculated but excluding the 30% outliers. Finally, the 30% outliers were again removed and a linear function of μ_f was calculated as shown in Figure 25. The simulated results are shown and compared with the experimental values in Figure 26. It can be seen that no method resulted in a perfect match. This is not surprising as the experimental values were not completely consistent. The value for R_{tot} varied considerably between the experiments, as seen in Figure 24. However, from observing Figure 26, it can be concluded that expressing R_{tot} as a function of the feed viscosity resulted in the best curve fit. For further simulations, R_{tot} was therefore chosen as $R_{tot}=f(\mu_f)$.

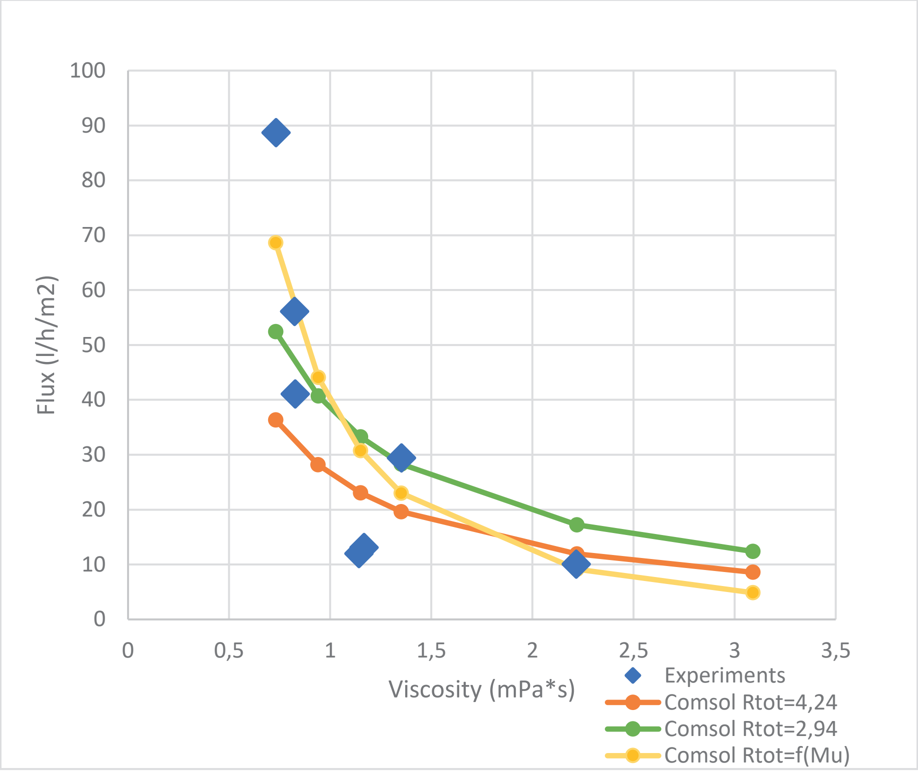


Figure 26. Experimental values for flux compared to simulated Comsol results.

To study the effect of viscosity on the flux in the M39, a material function for viscosity as a function of concentration and temperature was done by measuring the viscosity of different temperatures and concentration of molasses. Solutions of between 10 to 50 wt-% molasses were prepared and viscosity was measured at 25 and 50 °C. Results were plotted in Comsol and are presented in Figure 27. This allows Comsol to interpolate anywhere between the measuring points and linearly extrapolate beyond them. Therefore, Comsol could find a viscosity value for any concentration and temperature in the measured range. However, there is a risk of extrapolation outside the measured range.

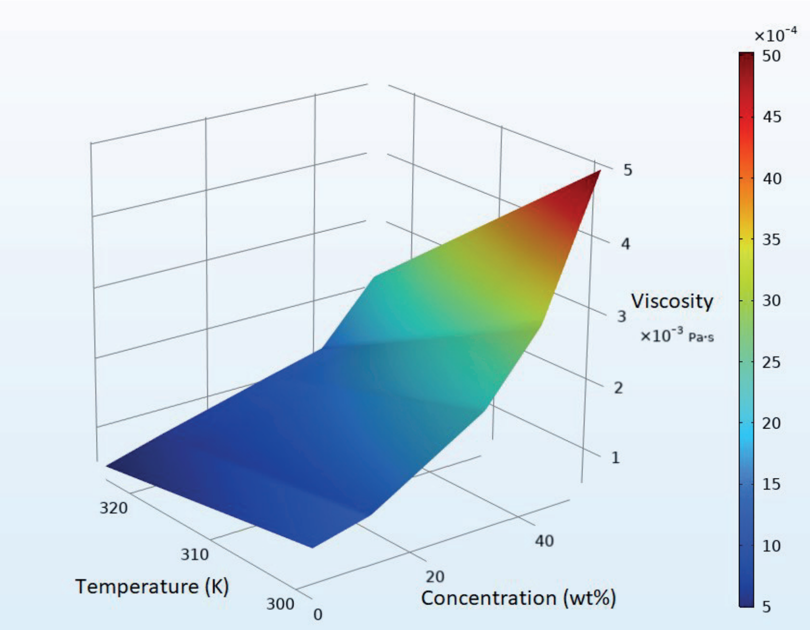


Figure 27. Viscosity in molasses as function of temperature in Kelvin and mass percentage molasses.

6.2 Simulation Results

6.2.1 Base case

A small cross section of the lower part at the end of a much longer M39 plate module is shown in Figure 28. The flux exits the module at the top and bottom and passes through a thin membrane at the boundary. A thin boundary layer of approximately 10 µm thickness can be observed where the concentration is higher than in in the bulk solution. This is then formed since the membrane prevents some particles from passing through the membrane. However, by looking at the scale it can be concluded that this layer is less than 1% more viscous than the feed. Hence the simulation showed little interference for the flux by any viscous boundary layer. Figure 28 (a) shows the 10 wt-% case while Figure 28 (b) shows the viscosity profile for a much more viscous 50 wt-% molasses feed. Although the viscosity is higher in the 50 wt-% case, the two viscosity profiles are very similar. This may seem surprising, however when Comsol calculates the flux by using Equation (8), any increase in viscosity in the module is cancelled out by a sharp decrease in flux, as shown in Figure 28. For comparison, a simulation was done where the TMP was increased from 3 to 15 bar. This resulted in a more pronounced viscous boundary layer as shown in Figure 28(c), However, the reduction in flux caused by this boundary layer was still less than 1% in Comsol compared to a scenario where the boundary layer was ignored. The transmembrane pressure required for this case would not be realistic for this particular set-up with the M39 module.

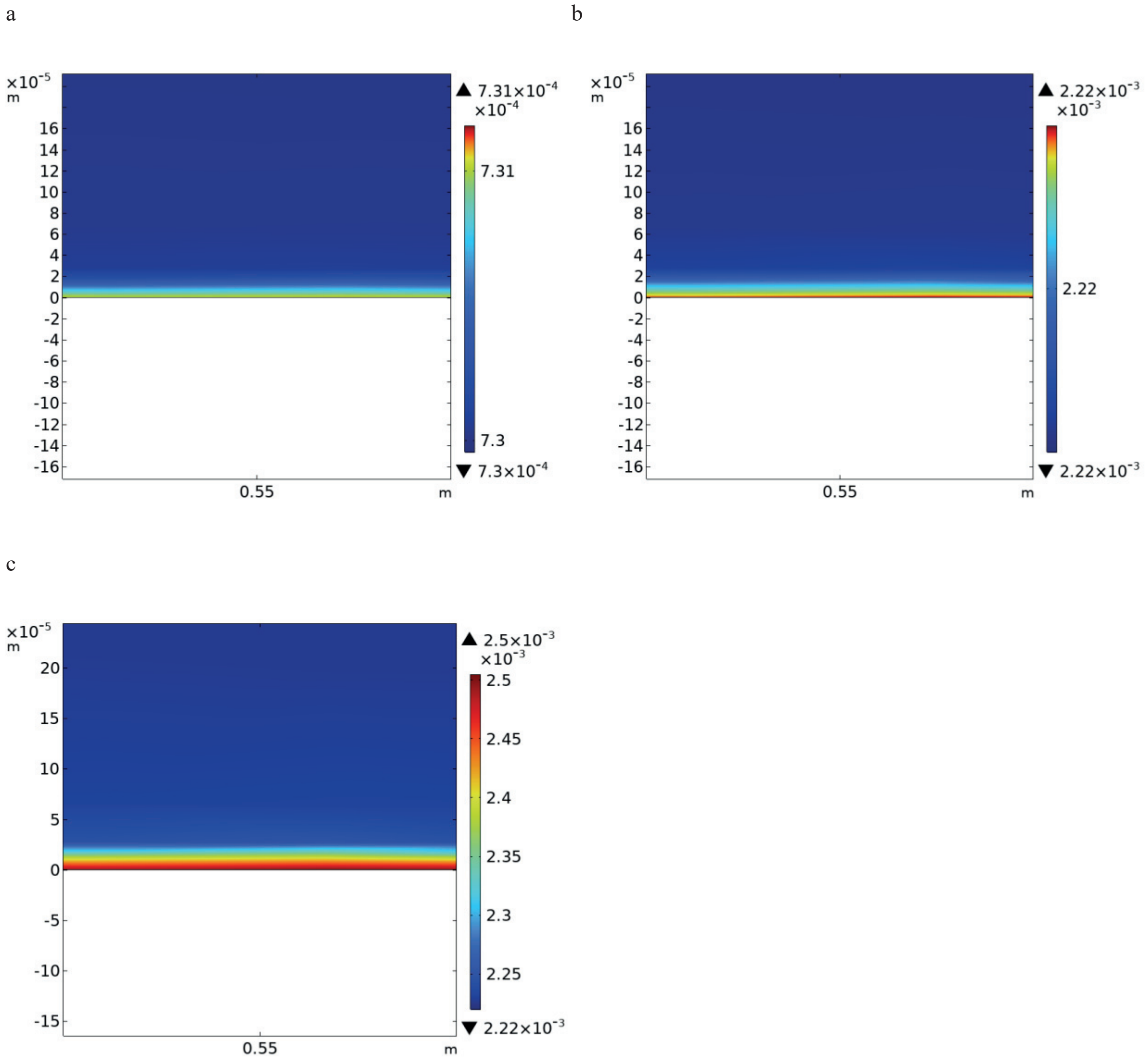


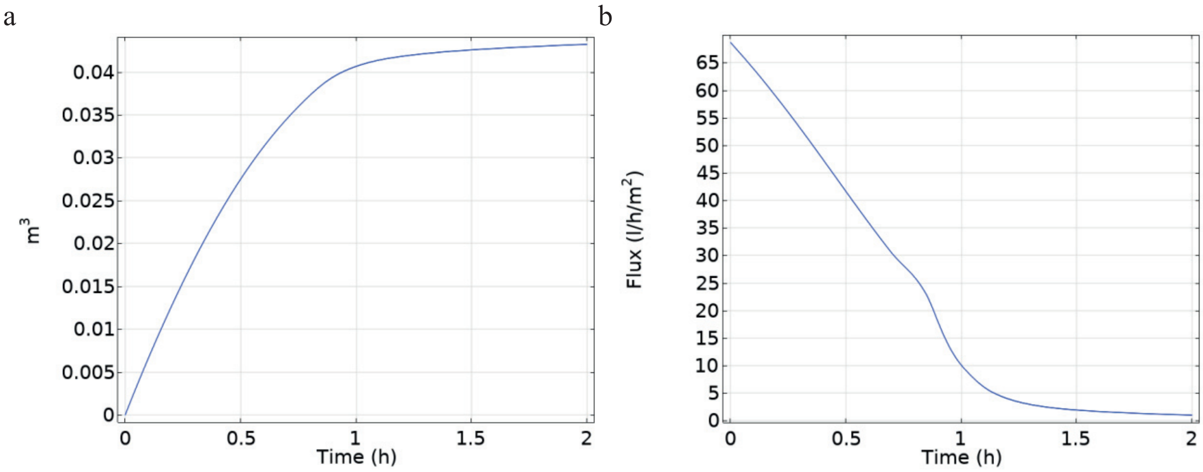
Figure 28. Cross section at the end of a M39 channel. Membranes located at top and bottom. Viscosity profile for 10 wt-% (a) and 50 wt-% (b) profile for steady state case, as well as 50 wt-% with 60 bar TMP (c). Left y-axis shows height, right y-axis viscosity (Pa*s) and x-axis length. (note the difference in scale).

It can therefore be concluded that only when using very highly concentrated and viscous feeds, and extreme transmembrane pressures, the boundary layer viscosity can be a limiting factor for flux in this particular set up. The low retention in the membrane is likely to be a contributing factor.

6.2.2 Time dependent 50 L tank

The results of the time dependent study are presented below. During the total time of 2 hours, a total volume of approximately 43 litres was removed as seen in Figure 29 (a). The initial flux was 68 l/(h m^2) and after 2 hours it was less than 2 l/(h m^2) as can be observed in Figure 29 (b). The concentration of the final recirculated feed was just above 65 wt-%. Figure 29 (c) shows the retentate concentration over time. The increase of the viscosity in the feed tank over time can be seen in Figure 29 (d).

There is a noticeable change in the flux line in Figure 29 (b) after approximately 0,8 hours and followed by a more rapid decrease in flux over time. This might be explained by the sharp increase in viscosity at this time, as seen in Figure 29 (d) which is also well in line with the viscosity curve of molasses in Figure 13. The rate of concentration change in Figure 29 (c) can be seen to first increase and then decrease. This is likely due to the at first almost constant reduction rate in volume in the feed tank, see Figure 29 (a), affecting the concentration less while almost the whole 50 L tank volume is still present. As the tank volume is reduced, approximately after 0,5 hours, the flux is still high. However, each removed volume unit of permeate affects more the remaining tank concentration. As the flux sharply decreases after approximately 1 hour, the concentration in the tank is less affected since the volume reduction rate is now very low.



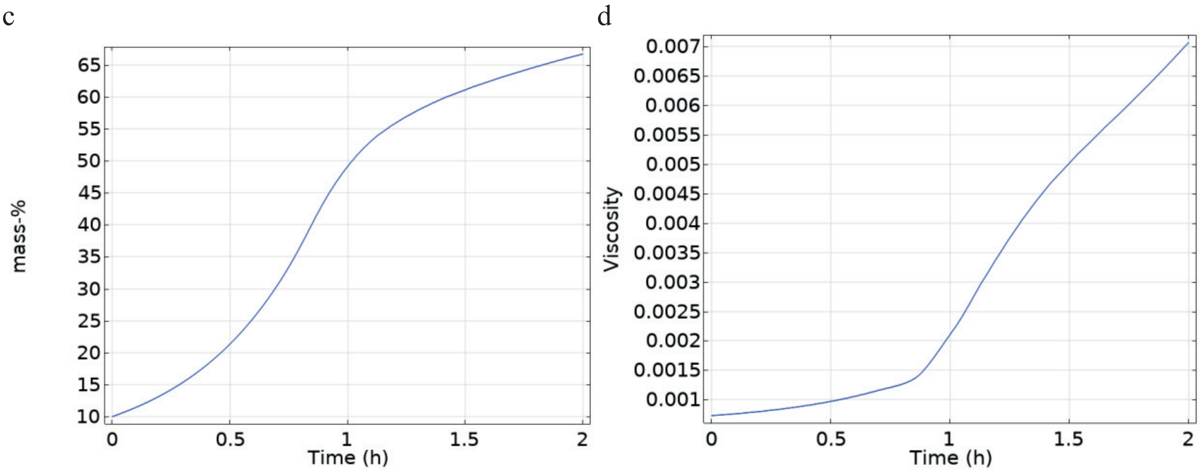


Figure 29. Total permeate volume (a), flux over time (b), concentration in wt-% in the feed tank (c), viscosity in the feed tank (d).

The flux dependency on viscosity, as well as wt-% concentration for the 50 L tank simulation can be seen in Figure 30. The results are well in line with experimental ones and show strong influence of viscosity on flux. The sudden change in the flux curve seen in the Figure 30 (b) at 40 wt% can be explained due to the earlier discussed sharp viscosity change in Figure 29 (d).

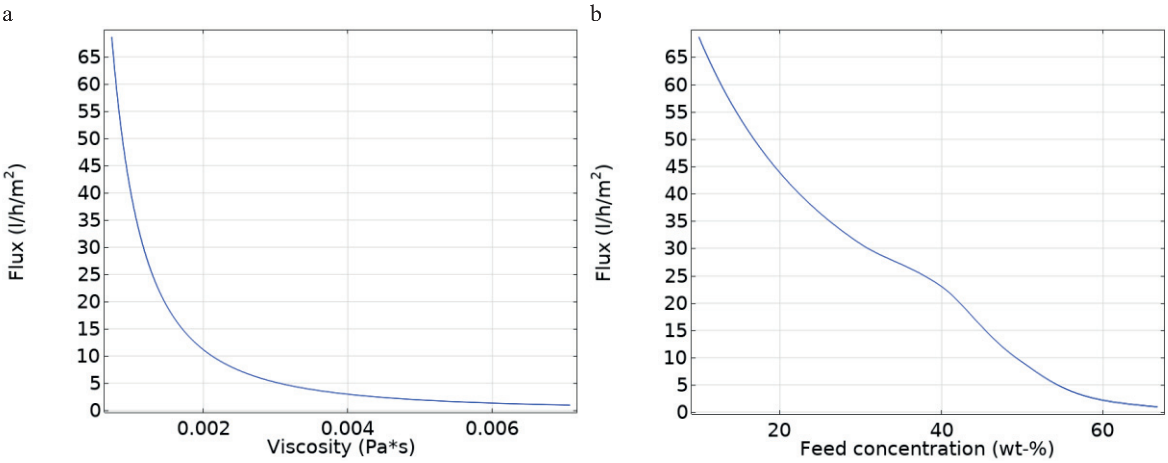


Figure 30. Flux against viscosity of the feed (a) and against feed concentration wt-% (b)

In Figure 31 (a) cross section of a small portion of the much longer M39 module is shown, with the membranes placed on the top and bottom. Figure 31 (a) shows the typical laminar velocity profile as calculated by Comsol with velocity ranging from 0 to 1 m/s. Figures 31 (b-c) show the concentration profile at different times during the simulation, with the concentration in wt-%. Very little concentration polarization was observed but as expected average concentration in the unit increased over time as low-concentration permeate was removed and the volume and therefore the concentration increased in the feed tank.

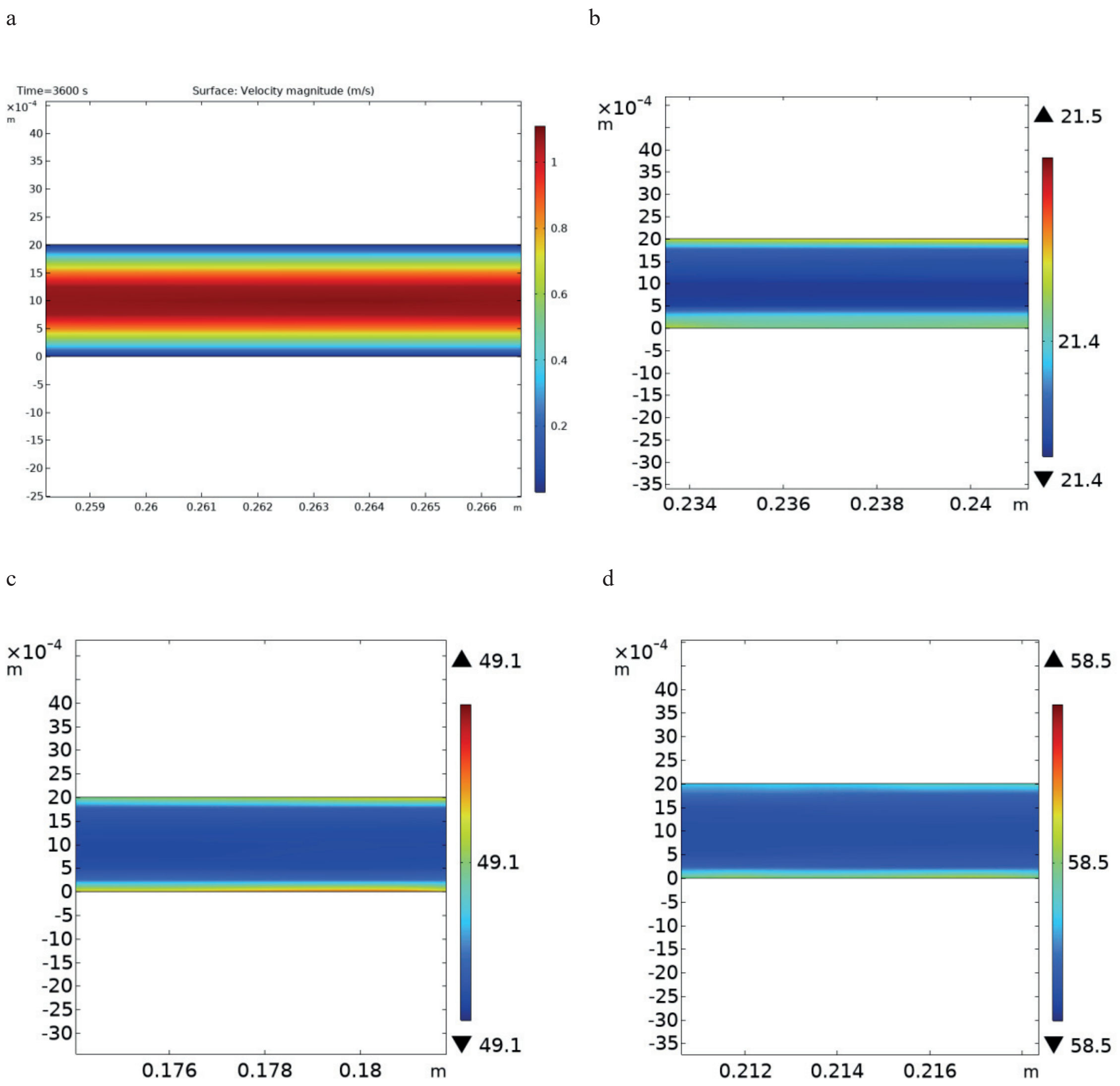


Figure 31. Velocity profile (a) after 1 hour and concentration profiles for part of the M39 unit at 0,5 h (b), after 1 h (c) and after 1,5 h (d). Left y-axis is height, right y-axis concentration in wt-%. X-axis length.

6.2.3 Flux dependence

Finally, the model was used to simulate a number of fluxes for different concentrations and temperatures. Four different temperatures between 25 and 55 °C were used, and a parameter sweep was done for concentrations from 10 to 60 wt-%, each step a 10% increase. Results are presented in Figure 32 and it shows the strong effect of temperature and concentration on viscosity and therefore flux. Results are in line with the known effect of temperature on flux, as shown by Howell et al. [2]. The reason is the strong temperature dependence of viscosity. As viscosity is reduced with increasing temperature the result is an increase in flux, as can be concluded from Equation (2).

The results from the simulation might be used to predict a flux at a certain concentration and/or temperature. Furthermore, the results could suggest what increase in temperature would be required, when there is a demand to maintain a constant flux with increasing concentration.

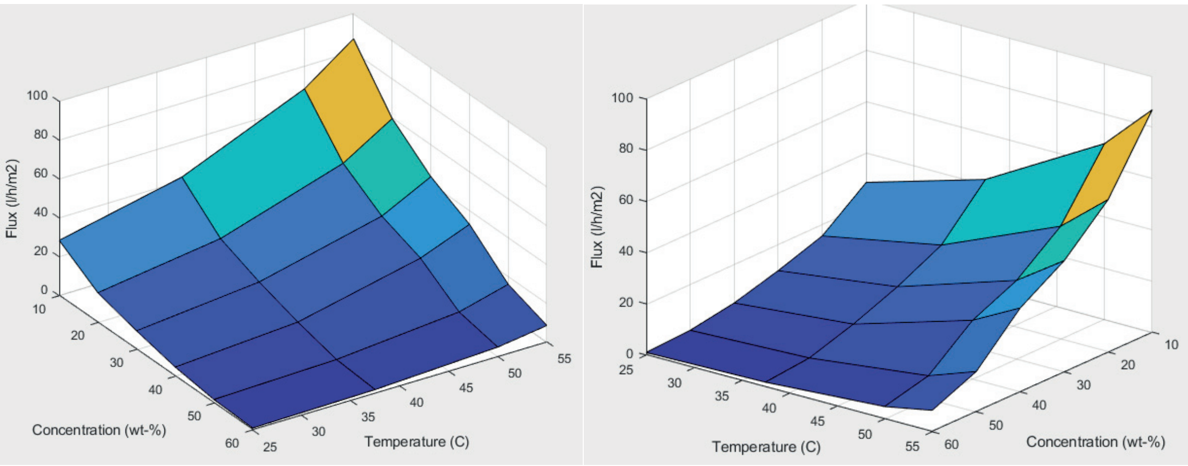


Figure 32. Flux against concentration and temperature. Same surface plot from two different angles.

7. Discussion

7.1 Operational experiments

During the experiments, a number of unexpected results were obtained. Especially outstanding were the low fluxes for the two 30% concentration experiments with molasses. Another value which was a possible outlier was the flux value for the 40% molasses concentration, which was relatively high compared to other values as seen in Figure 15. Possible explanations for these unexpected results may come from the handling of the Alfa Laval Combi M39/3.8 pilot unit. Keeping the flow rates completely steady during the experiments was sometimes challenging. Whenever using the auto-flow function of the pump, care would have to be taken that there always was sufficient liquid available for the pump. If this was not the case the pump would react strongly in its attempt to draw in more liquid to compensate. This could result in a large increase in flow rate and as a result in pressure. However, although this could present a problem when initializing an attempt, once a steady state was attained, there was no problem of this sort. For future attempts with the Alfa Laval Combi M39/3.8 pilot unit it should be noted that any volume under 20 l risks operational malfunctions, and this risk increase if the volume is less than 15 l. Furthermore, a lower flow rate will result in steadier experiments and going above 4 m^3/h is not advised when using the M39 module. In general, a higher flow rate requires a larger volume to avoid the pump sucking air. For the outlying 40% molasses value the reason for the relatively high flux compared to other concentrations might be that the membranes had so far not experienced much fouling, as this was only the second experiment.

Another unexpected issue was the automatic flux measurer, which proved unreliable when measuring intermediate fluxes below 50 $l/(h\ m^2)$, and stopped reporting values under 10 $l/(h\ m^2)$. Therefore, low fluxes had to be measured by hand with a measuring cup and a timer, and a calibration curve had to be done, which translated automatically logged fluxed into real fluxes, to obtain accurate and comparable results.

Keeping a steady temperature demanded constant attention and fine tuning. It was observed that the temperature was almost always either climbing or descending. In fact, once the required temperature of 50 °C was reached, little or no further heating was required, as the pump supplied sufficient heat to the process. Instead, a steady source of cooling was needed.

7.2 Discussion of results

The decided order of experiments for different concentrations of molasses resulted in some unexpected results. The second experiment with a 40% molasses solution resulted in unexpectedly low permeate flux compared to the previous experiment with 10% molasses. The reduction in permeate flux was about 75%. To collect data to understand this sharp decline, the decision was made to attempt concentrations between 10% and 40% which were initially excluded.

The first experiment at 30% molasses resulted in an unexpectedly low flux as this flux was lower than the flux at 40% molasses. The experiment was then repeated a second time but the result was approximately the same. It was speculated that the likely cause of this was the irreversible fouling of the membrane during experiments despite cleaning, or simply incorrect handling of the M39 and the dilution of the molasses during the experiment. In Figure 34 (c), Appendix A, a sharp initial decrease and then a partial recovery can be observed. It can be speculated that the cause of this initial decrease and then recovery, which was not seen for any other molasses experiment, was insufficient mixing during the dilution of the molasses, leading to fouling of the membrane. Another explanation for the 30% molasses experiment, compared to higher concentration fluxes, is the beginning of a limiting flux where flux after a certain concentration no longer decreases, as described by Shu-Sen [12] and Aimar et al. [13]. If this was the case then the flux at 40% would be the outlier by being too high compared to the fluxes for concentrations at 30%. In hindsight, the experiment at 40% could also have been repeated to see if a second experiment would have given a value closer to the 30% flux, in which case it would have been likely that there was indeed a limiting flux present already at the 30% molasses flux. If the value for 40% molasses is removed as an outlier, there would be a clear resemblance between Figure 2 [12] and Figure 15, strengthening the hypothesis of a limiting flux in this case.

However, no particular faults in the execution of this experiment could be identified. A second attempt at 30% was also done with extra care taken for each step. This attempt however gave almost identical results, strengthening the hypothesis that experiments were performed with good repeatability. A possible explanation for achieving the same result could be that although the experiment was performed well, fouling had occurred after the last experiment and the standard membrane cleaning was not sufficient in this case. In conclusion, the best course of action when performing this type of experiment would be to go from lower to higher concentrations, use large volumes, and make sure that all solutions are homogenic with regard to concentration and temperature by rigorous stirring.

Interestingly, a decrease and then an increase of flux with concentration, as observed with the molasses is not unknown in the literature. Pritchard et al. observed the same flux appearance for a flat sheet membrane module with a feed of xanthan gum [11]. When observing Figure 15 and comparing it to Figure 33, there is a quite similar change in how the flux first decreases, and then increases with concentration in the feed. However, in the experiment with xanthan gum the flux behaviour was attributed to shear thinning reducing the effect of concentration polarisation at the membrane surface, which seems to be unlikely to be the case in this study, as retention was very low and hence it was assumed that not much concentration polarisation was present.

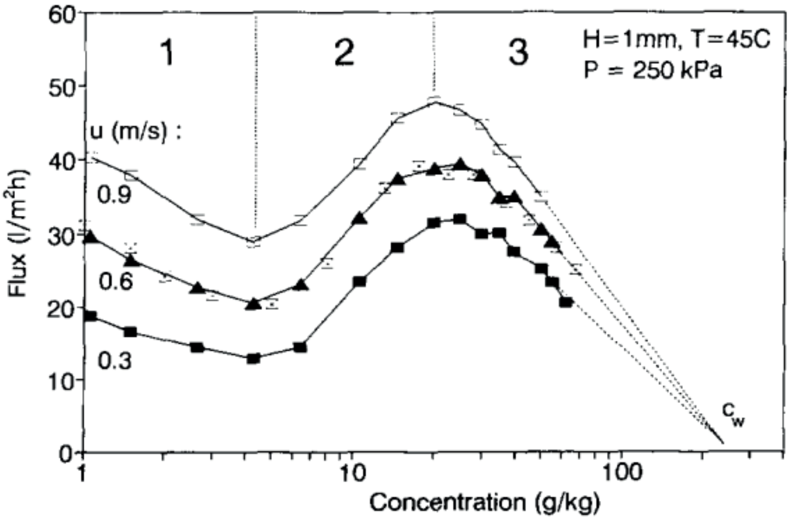


Figure 33. Flux compared to xanthan gum concentration for different flow rates. Figure from Pritchard et al. [11]

When considering further experiments on the effect of viscosity on membrane flux, there are many possibilities. Other substances than molasses could be used. Any substance where there is a combination of viscosity increasing with concentration as well as manageable fouling could potentially be of interest. One such molecule may be polyethylene glycol (PEG) or a different polymer. Another possibility would be to study the effect of temperature on the flux, when keeping the concentration constant as viscosity is highly dependent on not only on the concentration of the substance studied, but also on the temperature. Another interesting possibility could be to consider a similar set-up and feed, but use a membrane of a different material or MWCO. Broadly speaking, there are typically two approaches to membrane filtration of molasses. UF, to separate macro molecules in the retentate, and NF to concentrate sucrose. A more complete application involving membrane filtration of molasses may well need to include both UF and NF.

KGM offered substantially greater challenges compared to molasses when cleaning was concerned, as the PWF was severely reduced after each experiment, and a number of both acidic and alkaline cleanings was then required. The cleanings required a larger amount of time as well as a slightly higher cleaning temperature. Still, it was not always possible to recover the previous PWF.

It can be concluded that for the molasses experiments, the main flux reducing concentration dependant factor was the permeate viscosity, while the membrane hydraulic resistance (R_{tot}) had only limited influence. For the KGM experiments, the reverse relation was observed. The high retention for the KGM resulted in little concentration dependence of the viscosity of the permeate. In fact, the permeate had almost the same viscosity in all experiments. The R_{tot} value however showed a strong feed concentration dependency. The likely reason for this is a compaction of the cake layer, where the large, high molar mass, KGM molecules over time attach to the membrane and make it more difficult for the permeate to pass through.

The performed UF could handle considerably higher concentrations in the molasses experiments compared to the KGM experiments. For KGM, even low concentrations in the range of 1 g/l led to considerable reduction in flux as well as serious fouling. The reason might be that the high molar mass and long chained structure of the KGM molecules were effectively retained by the membrane. The low molar mass, small molecules in the molasses on the other side passed to a large degree through the membrane.

The simulations results suggested that there was little concentration polarization for the particular set-up. This might be due to the low transmembrane pressure resulting for most concentrations in a relative low flux. Crossflow velocity was also quite high, resulting in a short residence time in the M39 module for the liquid. Another reason might be the low retention of the RC70PP UF membranes. When a small volume with almost the same composition as the feed, is diverted as permeate, the composition of the remaining liquid will change very little. Although concentration polarization was not an issue in this case. Furthermore it might be of interest to know concentrations throughout the M39 module, for example if there is a risk of precipitation or if a saturation concentration is reached, which could be the case locally. The simulation results might be of some value for this application or a similar set up using NF. For example, it could answer questions such as how long it would take to concentrate a given volume into a higher concentration, or how much product is lost with the permeate at a given retention. The strong temperature dependency of the viscosity and therefore the flux were successfully modelled, and may answer what temperature is required to maintain flux at higher concentrations. If a certain process calls for a constant flux, temperature could be slowly increased to counterbalance a decrease in flux as concentration increases.

8. Conclusion

When investigating the flux dependence on viscosity in this study, it was concluded that for molasses, the most important factor was the permeate viscosity, while for the KGM the permeate viscosity was almost the same for all experiments, and the most important factor was instead the R_{tot} value.

The investigation of the boundary layer at the membrane surface by Comsol simulations showed little concentration or viscosity polarization for the molasses feed. This may be in line with actual reality, but it is also likely there are other more complicated interactions which the model failed to account for. A solute with such low retention as molasses had in this study which therefor does not create much concentration polarization is not well suited for Comsol simulations in this regard.

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Appendix A: molasses flux curves

The flux curves for molasses are shown in Figure 34. Flux decreases with concentration. The two 30% flux curves had unexpectedly low fluxes.

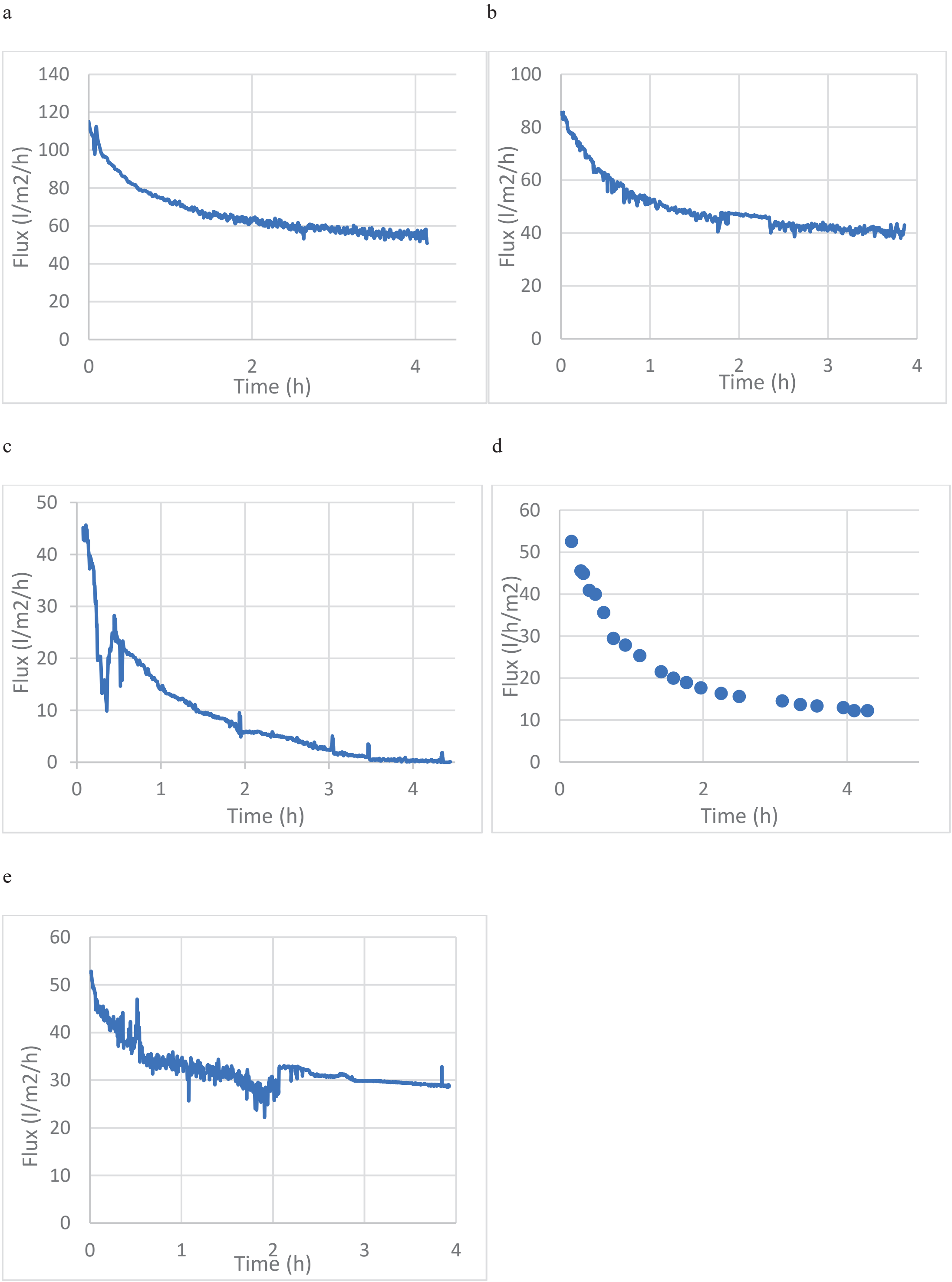

Figure 34. Flux charts for molasses, (a) 15%, (b) 20%, (c) 30 % automatic, (d) 2nd 30% manual and (e) 40%,

Appendix B: KGM flux curves

Flux charts for KGM are shown in Figure 35. Flux was more stable over time compared to the flux curves for molasses, but the short time-variance in flux was also greater.

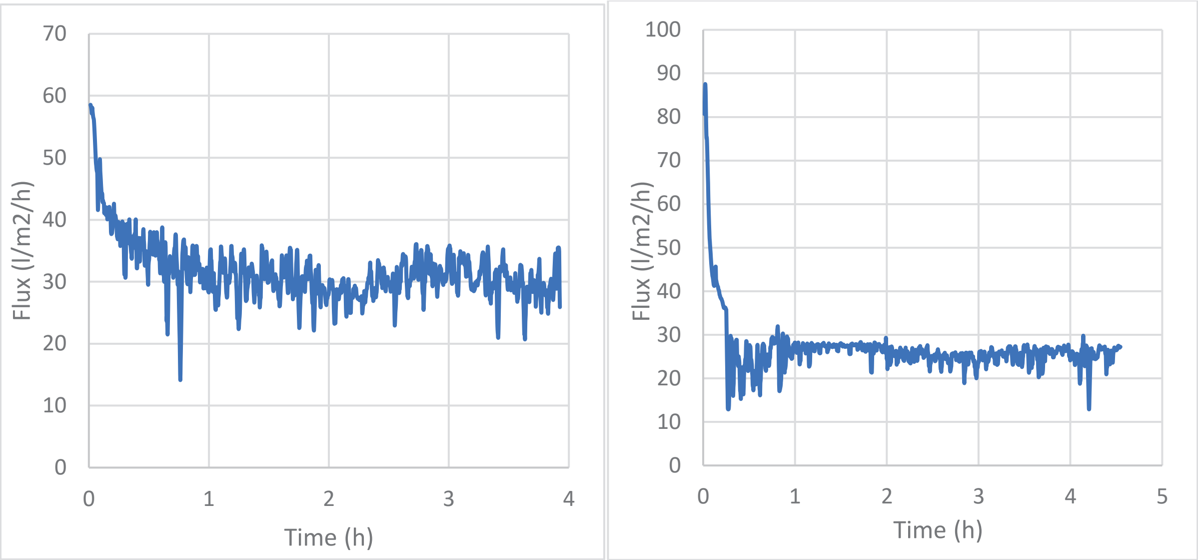

Figure 35. Flux charts for KGM 0,3 g/l (left) and 0,5 g/l (right).

Appendix C: Molasses retention

Retention data for molasses is shown in Table 4. Retention was generally low with an average value of about 3.5% for Brix and 5.2% for viscosity.

Table 4. Brix and viscosity for feed and permeate for all experiments with 100% as a reference value.

Approx. conc.	**Real conc.**	**Brix (°Bx)**				**Viscosity (mPa*s)**				**Flux (l/(h m^2))**
		Feed 0h	**Feed 4h**	**Perm- 0h**	**Perm- 4h**	**Feed 0h**	**Feed 4h**	**Perm. 0h**	**Perm 4h**	
10%	8%	6.5	6.6	6.3	6.4	0.86	0.73	0.71	0.71	88.7
15%	13%	10.4	10.7	10.0	10.2	0.87	0.82	0.79	0.77	56.1
20%	15%	11.5	12.0	11.0	11.5	0.81	0.83	0.78	0.83	41.1
30%	28%	21.8	22.2	21.0	21.3	1.16	1.14	1.11	1.07	12.0
30% (2)	29%	22.5	23.0	21.3	22.0	1.14	1.17	1.06	1.09	13.1
40%	34%	26.5	27.1	25.7	26.4	1.33	1.35	1.23	1.26	29.4
50%	46%	35.6	37.0	34.8	36.4	2.03	2.22	1.88	2.03	10.1
100%		78.2								

Appendix D: KGM retention

Retention data for KGM is shown in Table 5. Retention varied substantially due to small experiment samples. Retention was estimated to be 80%.

Table 5. Dry weight and retention for KGM

Conc.	Liquid	Wet weight	Dry weight	Dry part	Retention
0.3 g/l	F-0h	9.7917	0.0036	0.00037	
	P-0h	9.8967	0.0029	0.00030	17.6%
	F-4h	9.8556	0.0037	0.00038	
	P-4h	9.8650	0.0011	0.00011	70.3%
0.5 g/l	F-0h	9.9228	0.0057	0.00057	
	P-0h	9.8870	0.0029	0.00029	48.9%
	F-4h	9.9444	0.0048	0.00048	
	P-0h	9.8737	0.0008	0.00008	83.2%
0.85 g/l	F-0h	9.7774	0.0098	0.00100	
	P-0h	9.9006	0.0019	0.00019	80.9%
	F-4h	9.7348	0.0106	0.00109	
	P-4h	9.8853	0.0022	0.00022	79.6%

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