TÉCNICO LISBOA

Separation of Sugars by Ceramic Nanofiltration Membranes

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Resumo

O açúcar, na forma de sacarose, é um dos produtos mais consumidos nos dias que correm e o seu processo de extração encontra-se já bastante estudado. Os melaços são um subproduto deste processo, com alto teor de sacarose, ainda por extrair. A recuperação de sacarose presente nos melaços encontra-se em desenvolvimento e é necessário investigar novos metódos para tal. É neste âmbito que os processos de separação via membranas podem contribuir para um desenvolvimento processual e económico deste processo.

O presente projecto consistiu na avaliação da utilização de um processo de nanofiltração com membranas cerâmicas para a recuperação de sacarose presente nos melaços produzidos no processamento da beterraba sacarina. Duas membranas com MWCO de 200 e 350 Da foram testadas sob diferentes condições operatórias.

A Membrana LC1 mostrou ser a mais adequada para a execução da separação pretendida, apresentando elevados fluxos de permeado e altas retenções de sacarose. Esta membrana apresentou uma permeabilidade hidráulica de 28.2 L/m^2hbar. O fluxo de permeado rondou os 250 L/m^2h e a retenção de sacarose os 80%, quando se operou a 70°C, com CFV de 1 m/s e TMP de 10 bar.

Palavras-chave: Beterraba Sacarina, Melaços, Sacarose, Nanofiltração, Membranas Cerâmicas.

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Abstract

Sugar as sucrose, is one of the most consumed products nowadays and its extraction process is already well studied. Molasses are a by-product of this process, which have a high content of sucrose, yet to be extracted. Recovery of sucrose from molasses is in development and it is necessary to investigate new methods suitable for such. It is in this context that the membrane separation processes can contribute to an economic development of this process.

The aim of the project was to evaluate the performance of a nanofiltration process using ceramic membranes to recover sucrose from sugar beet molasses. Two membranes with MWCO of 200 and 350 Da were tested under different operating conditions.

Membrane LC1 was the most adequate to reach the project objective, presenting high permeate fluxes and high levels of sucrose retention. This membrane had a hydraulic permeability of 28.2 L/m^2hbar. The permeate flux was around 250 L/m^2h and the retention of sucrose was 80%, when operated at 70°C, a CFV of 1 m/s and a TMP of 10 bar.

Keywords: Sugar beet, Molasses, Sucrose, Nanofiltration, Ceramic Membranes.

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Glossary

CFV	Cross-Flow Velocity.
HPLC	High-Performance Liquid Chromatography.
MF	Microfiltration.
MW	Molecular Weight.
MWCO	Molecular Weight Cut-Off.
NF	Nanofiltration.
PWF	Pure Water Flux.
RI	Refractive Index.
RO	Reverse Osmosis.
SEC	Size-Exclusion Chromatography.
TMP	Transmembrane Pressure.
TS	Total Solids.
UF	Ultrafiltration.
UV	Ultraviolet.
VR	Volume Reduction.

Symbols

ΔP	Transmembrane pressure.
μ	Viscosity.
Π	Osmotic pressure.
ε	Membrane porosity.
τ	Tortuosity factor.

C_b	Concentration in the bulk solution.
C_m	Concentration at the membrane surface.
C_p	Concentration in the bulk solution.
D	Diffusion coefficient.
F_a	Degree of fouling after cleaning.
F_b	Degree of fouling before cleaning.
J	Flux.
J_w	PWF of cleaned membrane.
J_{w*}	PWF of fouled membrane.
J_{wi}	PWF of new membrane.
k	Mass transfer coefficient.
L_p	Hydraulic permeability.
L_{pw}	Hydraulic permeability of cleaned membrane.
L_{pw*}	Hydraulic permeability of fouled membrane.
P_{feed}	Pressure of the feed.
P_{perm}	Pressure of the permeate.
P_{ret}	Pressure of the retentate.
R_a	Adsorption resistance.
R_{cp}	Concentration polarisation resistance.
R_{fc}	Filter cake resistance.
R_g	Gel-layer resistance.
R_m	Membrane resistance.
R_{obs}	Observed retention.
r_p	Pore radius.
R_p	Pore block resistance.

R_{true} True retention.

V_{feed} Volume of the feed.

V_{perm} Volume of the permeate.

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1 Introduction

1.1 Motivation

Sugar is an important form of carbohydrates that is widely consumed and can be found primarily in fruits and vegetables. Due to its properties, sugar has many applications such as sweetening, preservation and production of ethanol. The sugar sucrose can be produced from sugar cane or sugar beet. In geographic regions with moderate climates, the production of sugar from sugar beet is preferred due to the existence of more suitable climatic conditions for its cultivation. Nowadays, this process is well developed, but it is important to continue developing new technologies that allow a good efficiency and a lower energy consumption.

The sugar extracted from sugar beets is composed by different types of sugar molecules, such as mono- and disaccharides. So far, the bulk of sucrose is recovered through crystallisation but the separation of sugars from residues, such as molasses, has been accomplished through chromatography. However, that process presents a series of disadvantages since it requires a large amount of time, eluent and energy.

In recent years, nanofiltration has been considered as a promising alternative technology for the separation of sugars. When compared with chromatography, the nanofiltration process overall demands no eluent, consumes less energy and is faster. An important challenge for an efficient separation of sugars by nanofiltration is the selection of suitable membranes. There has been a great deal of commitment in the development and improvement of ceramic nanofiltration membranes, which are considered to have great potential for the separation of sugars due to their high durability, resistance to high temperatures and bacterial resistance.

Therefore, this project will focus on testing ceramic nanofiltration membranes to perform the separation of sucrose from fructose/glucose solutions which would enable purification of sucrose from molasses. In addition, an attempt will be made to find suitable operating conditions.

1.2 Objectives

The project aimed for the following objectives:

- Chemical and physical characterization of a sample of beet molasses;
- Selection of a suitable membrane and operating conditions through parametric studies;
- Analysis of the influence of temperature on the separation.

1.3 Thesis Outline

This thesis will be divided into four distinct sections:

1. **Literature Review** - The chapter is a summary of the bibliographical studies and aims to provide the background necessary for understanding the project.
2. **Experimental Work** - All the information regarding equipments, experimental set-ups and procedures are explained in this chapter. The experiments were performed in the Department of Chemical Engineering, Lund University, Sweden.
3. **Results and Discussion** - The obtained results are presented, analysed and discussed in this chapter.
4. **Conclusions and Future Perspectives** - The last part of the report focuses on concluding remarks and suggestions for future work.

2 Literature Review

2.1 Sugar Industry

The sugar industry subsumes the production, processing and marketing of sugar, in the form of sucrose, that can be extracted from sugar cane or sugar beet. Sugar cane, on average, accounts for about 80% of the global sugar production, with the remainder being produced from sugar beet. In Table 1, some data on the global production of cane sugar and beet sugar in the year of 2016 is presented.

Table 1: Global production of cane sugar and beet sugar in 2016 [1].

Cane Sugar		**Beet Sugar**	
Producers	Mton	Producers	Mton
Brazil	39	EU-28	15
India	25	Russia	6
Thailand	9	USA	4
China	9	Turkey	2
Mexico	6	Ukraine	2

As mentioned earlier, this project is focused only on sugar beet, more specifically on a by-product derived from its processing, beet molasses. Hence, it is important to know how the sugar beet is processed industrially, the operating conditions and its products and by-products. A schematic illustration of a beet sugar processing plant is shown in Figure 1 and it is preceded by a detailed description of the process.

The production of beet sugar starts with washing and slicing the sugar beets into "chips". The "chips" are then processed in the diffuser where the extraction of the raw beet juice occurs, leaving as a byproduct the beet pulp, which is used as cattle feed, to produce ferrulic acid (a percursor of vanillin, which is a high valuable product). The water temperature in the diffuser is typically maintained at 70°C and this step lasts for 100 min. Liming, carbonation and demineralization of the raw beet juice is applied in order to remove proteins, pectins, inorganic salts, and coloring substances and it is performed at 75-95°C for 60 min. Afterwards, the purified thin juice is concentrated by multistage evaporation for 100 min at 98-130°C resulting in a thick juice composed by 50-65% of sucrose. The last step is the boiling and crystallization of the thick juice which leads to the separation of beet sugar and beet molasses. The crystallization is performed at 65-75°C and it takes 3-4 h [12] [21] .

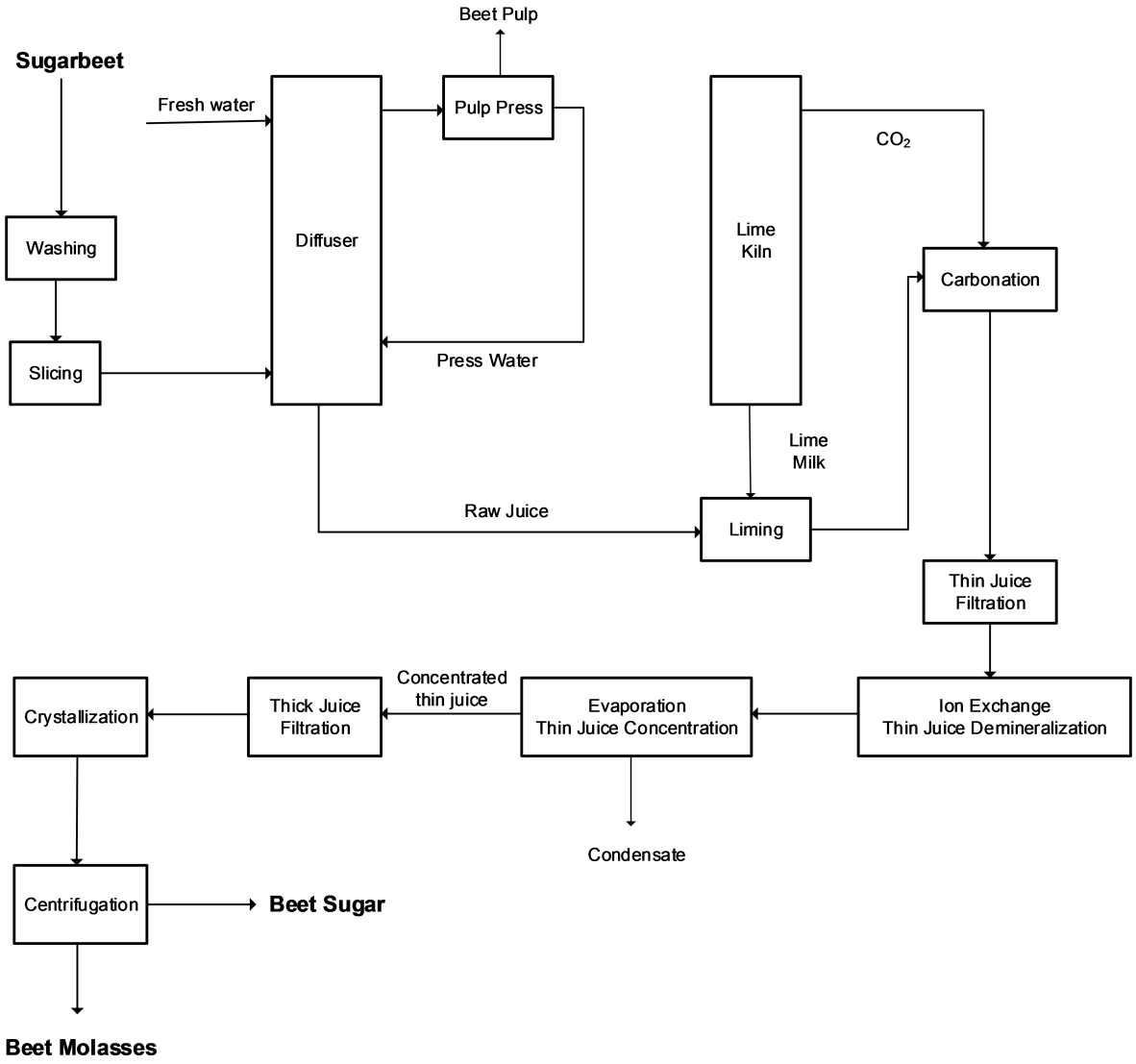


Figure 1: Schematic representation of a beet sugar processing plant. Adapted from [21].

Beet molasses is a byproduct of beet sugar production, and because of its potential for additional sugar recovery, it is the product that this work is focusing on. The total sugar content in beet molasses is approximately 50% , out of which 49% is sucrose and 1% is glucose, fructose and raffinose. Furthermore, molasses contains 4% organic acids predominantly lactic acid [12]. The sugar recovery from beet molasses, also known as molasses desugarization, is usually achieved by ion exclusion chromatography and allows the production of a 90 to 93% pure sucrose syrup extract [2]. In the current work, the possibility of recovering sucrose from beet molasses using ceramic nanofiltration membranes was studied. The membrane process seems to be a promising alternative to the conventional process due to the advantages already described in Section 1.1. Sections 2.3 and 2.4 focus on membranes and membrane processes, with the aim of giving a broad understanding on these topics.

2.2 Nanofiltration for Recovery of Sugars

In the last years many studies have been performed in order to assess on the use of membrane processes to separation and recovery of different sugars.

Nihal, et al., studied the effect of operating parameters on the separation of sugars by nanofiltration. Fist, it was study the separation performance of sucrose and glucose as individual solutions and then the separation performance of a binary solution of sucrose and glucose. Two different types of asymmetric polyamide membranes with 500 MWCO (Berghof, BM5) and 200 MWCO were used during nanofiltration experiments. It was observed that increasing the feed flow rate increased the permeate flux and rejection by minimizing the effect of concentration polarization. Increasing the pressure did not affect rejection significantly. Only in the low range did an increase in solute concentration caused important decreases in permeate flux and increases in rejection. The results indicated that a mechanism for the separation of organics by nanofiltration can be based solely on molecular size. Studies with binary solutions demonstrated that solute-solute interactions affected the performance of nanofiltration membranes. Rejection of a smaller solute (e.g., glucose) was improved by the presence of a large one (e.g., sucrose) [11].

Feng, et al., studied the separation of galacto-oligosaccharides mixture by nanofiltration. Four spiral wound nanofiltration membranes were applied to examine the separation performance of commercial galactose-oligosaccharide (GOS) mixture with the specification of 18.8 wt% monosaccharide (17.9 wt% glucose and 0.9 wt% galactose), 44.8 wt% lactose and 36.4 wt% galactose-oligosaccharides. The four tested commercial membranes were 1812 spiral wound membrane modules. The membranes NF-2 (500-600 Da) and NF-3 (800-1000) were supplied by Sepro Co(USA), assembled by Shanghai Mosu Co.(China). The manufacturer and module manufacturer of NF-1812-50 (150-300 Da)were Dow Chemical (USA) and Beijing Ande Co. (China), respectively. HBRO-1812-2 (800-1000 Da) was made and assembled by Hebei R.O.Environment Tech. Co. (China) It was concluded that high pressure can induce serious fouling due to the compaction of the membrane layer, which inevitably results in high energy cost. Hence, operation pressure of lower than 8 bar was adopted to test the separation performance of the membranes with sugar solutions. The permeate fluxes and apparent rejection of sugars increased with increasing pressure for a given membrane. With increase of temperature, the permeate fluxes increased and rejections decreased when other parameters were fixed. On the other hand, both permeate fluxes and rejections of sugars decreased with increasing feed concentration. The selection of optimum NF membrane and operation conditions for a separation process was a compromise between the permeate fluxes and rejections of sugar [7].

Qi, et al., investigated the removal of furfural and concentration of monosaccharides by using two commercial nanofiltraton (NF) membranes with synthetic glucose–xylose–furfural solution as model. Two commercially available NF membranes obtained from Dow FilmTech, NF90 (90 Da) and NF270 (150 Da), were employed in the present study. The effects of main operating parameters such as feed, pH, permeation flux, tempera-

ture and feed concentration on the rejections of the three solutes, were studied. For both membranes, the rejections of the three solutes were significantly influenced by the operating conditions, such as feed pH and solutes concentration, permeation flux and temperature [14].

The possibility of nanofiltration in a demanding separation of a pentose sugar, xylose, from a hexose sugar, glucose, was studied by Sjoman, et al. Xylose is an intermediate product in xylitol production and glucose interferes in the process. Feed solutions were made of xylose and glucose in different mass ratios and total monosaccharide concentrations. The experiments were made with a DSS LabStak M20 (Alfa Laval Copenhagen A/S, Denmark) plate and frame filtration equipment. The membrane stack contained three different membranes (listed from bottom to top): Desal-5 DK (150-300 Da), Desal-5 DL (150-300 Da)(GE Osmonics, USA) and NF270(150-200 Da)(Dow Liquid Separations, USA). The results indicated that the separation of xylose from glucose by nanofiltration is possible to a limited extent. The observed monosaccharide retentions depend highly on permeate flux, and retentions increased to certain reproducible level as pressure and consequently flux is increased. The observed xylose retentions were from 0 to 80% and the glucose retentions were from 10 to 90%. The effect of total monosaccharide concentration on the observed retention is smaller than the effect of flux. The ratio of xylose to glucose in the feed had an influence on permeate flux and on xylose retentions. Xylose retentions decreased as the proportion of glucose increased in the feed. The higher the proportion of xylose in the feed the higher was the total permeate flux [16].

2.3 Membranes

Membranes play a central role in our daily life and have been used in different processes for a long time. They can usually be defined as a selective barrier between fluids and may be characterized according to their structure or even the material in which they are composed.

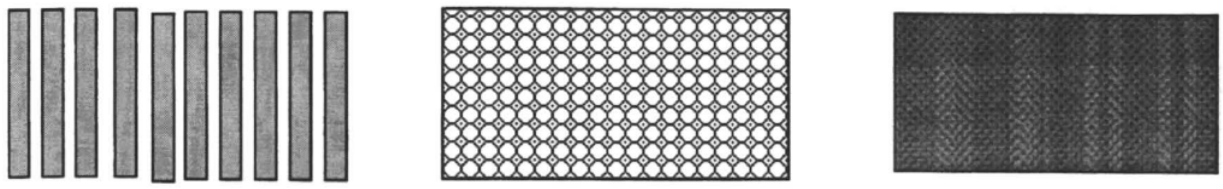
Thus, this sub-chapter will provide the essential knowledge on membranes, their structure and materials in order to facilitate understanding of the project.

2.3.1 Membranes Structure

Symmetric Membranes

Symmetric membranes are mainly used in processes such as dialysis, electrodialysis, and to some extent also in microfiltration and are defined as a membrane with uniform structure (uniform pore size or nonporous) throughout the entire membrane thickness [18]. This type of membrane structure presents a thickness usually between 10-200 μm [10].

In a symmetric membrane the structure and transport properties are identical over the entire cross-flow section and the total resistance of the mass transfer relies to the total thickness of the membranes [18].



(a) (b) (c)

Figure 2: Schematic representation of the cross section of symmetric membranes structures [13].

Asymmetric Membranes

Asymmetric membranes are used primarily in pressure driven processes such as reverse osmosis, ultrafiltration, or gas and vapor separation, since here the unique properties of asymmetric membranes, i.e. high fluxes and good mechanical stability can best be utilized. In this type of membranes, structure as well as transport properties vary across the membrane thickness. The asymmetric structure is composed by a 0.1-1 μm thick dense layer, also known as skin layer, supported by a highly porous, 100–200 μm thick support layer [18]. The dense layer provides the majority of selectivity for the membrane and the separation properties are determined by its chemical nature, size of pores (0.4–1 nm), and thickness [13]. The porous sub-layer serves only as mechanical support for the thin and fragile selective layer and it is considered to have a little effect on the separation characteristics and on the mass transfer rate of the membrane [18].

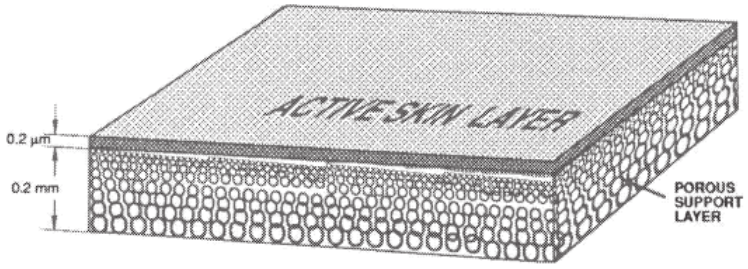


Figure 3: Asymmetric membrane structure [15].

Asymmetric membranes can be found in three basic structures: (i) integral-asymmetric with a porous skin layer, (ii) integral-asymmetric with a dense skin layer, and (iii) thin-film composite membranes [18].

2.3.2 Membrane Materials

Membranes can be made from a large number of different materials, but it is possible to divide them into three main categories: organic, inorganic and biological. Organic membranes are composed either by cellulose-based or polymeric materials. In contrast to this, inorganic membranes can be made from ceramic and metallic materials [10].

To achieve the best performance possible in the process, it is highly important to operate with a membrane material which has properties such as [15]:

- Chemical resistance (to both feed and cleaning fluids);
- Mechanical stability;
- Thermal stability;
- High permeability;
- High selectivity;
- Fouling resistant.

In this project, only the performance of ceramic membranes were tested. Thus, a special focus on this type of membrane will be given bellow.

Ceramic Membranes

The most common ceramic membranes are made of Al, Si, Ti, or Zr oxides and normally have an asymmetric structure composed of two or three different porosity levels, as shown in Figure 4. The active layer lies on the inside surface of the filtration channels and is in direct contact with the fluid to be treated, providing selectivity and an efficient separation. Between the active layer and the macroporous support, often, a microporous top layer and a mesoporous intermediate layer is applied in order to reduce the surface roughness. The macroporous support provides mechanical strength and simultaneously minimizes the mass transfer resistance [9] [17].

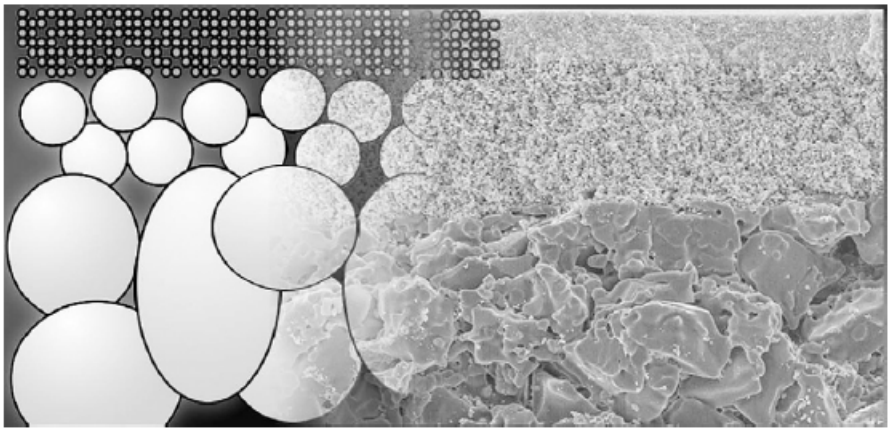


Figure 4: Schematic drawing combined with an electron microscopy image showing a cross section of a ceramic membrane (including the support) [9].

The ceramic membranes are usually formed into multichannel elements with different shapes, mainly round and hexagonal, and different channel diameters (Figure 5). This configuration provides higher membrane packing density and, consequently provides savings in capital and operating costs. These elements are then grouped together in housings, which are available in diverse materials such as stainless steel, coated steel, and plastics.

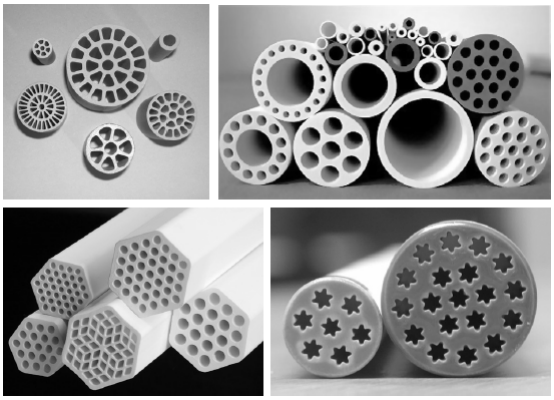


Figure 5: Examples of commercial ceramic membranes [9].

The application of ceramic membranes has been increased in different industries such as biotechnology and pharmaceuticals, dairy products, food and beverages. The main reason why ceramic membranes are becoming the preferred option for these industries is due to their high chemical and physical stability (thermal and mechanical), their separation characteristics and their long lifetime [9] [17].

When compared with other membrane materials used in pressure-driven membrane processes, the ceramic membranes present advantages such as:

1. High durability;
2. Resistance to high temperatures (up to 300°C) and high pressures (up to 30 bar);
3. Chemical stability (i.e., organic solvents, oxidants, ...)
4. High abrasion resistance;
5. High fluxes;
6. Bacterial resistance;
7. Easy cleaning and sterilization.

Ceramic membranes have a high weight and a high cost of production, which represents a disadvantage in their use. On the other hand, they hold a long life-time, up to 5 years when used for food industry applications.

2.4 Membrane Processes

All membrane processes have the common feature that separation is achieve via a selective barrier also called membrane. However, all these processes can differ greatly with regard to membranes, driving forces, applications, and industrial or economical relevance.

The driving force in these processes may be a pressure difference as in ultra-, micro- and nanofiltration or reverse osmosis, a concentration gradient as in dialysis and forward osmosis, or an electrical potential gradient as in electrodialysis. Given the current project, pressure-driven membrane processes will be the main focus.

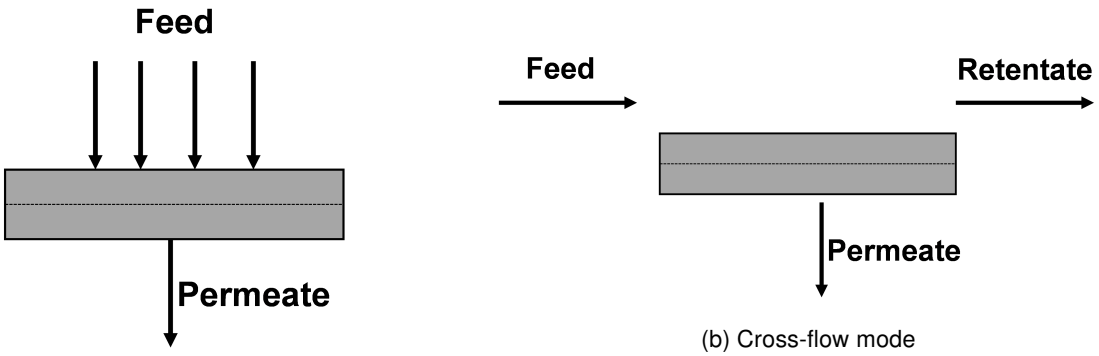
2.4.1 Pressure-Driven Membrane Processes

The most common pressure-driven membrane processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). All of these processes differ in some features, such as membrane structure, molecular weight cut-off (MWCO) and transmembrane pressure (TMP), as shown in Table 2.

Table 2: Pressure-driven membranes processes and technical features [4] [18].

Process	Membrane Structure	MWCO (kDa)	TMP (MPa)	Mechanism	Applications
Microfiltration (MF)	Symmetric and asymetric macroporous	>1000	0.05-0.2	Size exclusion; Convection	Water Purification; Sterilization; Separation of microparticles; Clarification
Ultrafiltration (UF)	Asymmetric macroporous	0.1-1000	0.1-0.5	Size exclusion; Convection	Separation of molecular mixtures
Nanofiltration (NF)	Asymmetric mesoporous	0.1-1	0.3-3	Size exclusion; Diffusion; Donnan-exclusion	Separation of molecular mixtures and ions
Reverse Osmosis (RO)	Asymetric skin-type; dense or microporous	0.01-0.1	1-10	Solution-Diffusion	Sea and brackish water desalination

Membrane processes can operate in two different modes: dead-end mode (Figure 6a) and cross-flow mode (Figure 6b). In the dead-end mode the feed is forced through the membrane by a pressure perpendicular to the membrane surface and, simultaneously, the retained particles begin to accumulate on the membrane surface to form a filter cake. This filter cake will increase over time to the point where the membrane is no longer feasible to perform the filtration and must be cleaned or replaced [10] [20].



(a) Dead-end mode

(b) Cross-flow mode

Figure 6: Schematic representation of membrane filtration operating modes [20].

The cross-flow mode has become the operating mode for filtration processes since it helps reducing the cake formation, and hence the lost of the membrane feasibility. In this mode, the feed stream flows tangentially to the membrane surface, and as result of the application of pressure force, the permeating species will pass through the membrane. Thus, the concentration of permeating species in the feed stream along the membrane will increase until it leaves the unit as retentate [10]. This mode of operation is presented in more detail in Figure 7.

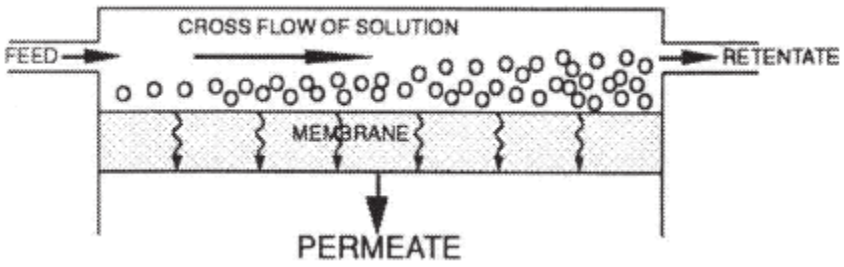
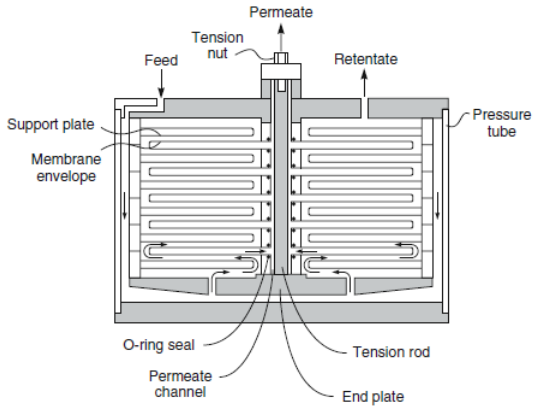


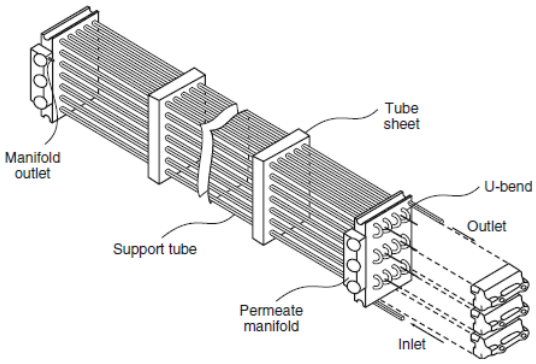
Figure 7: Cross-flow membrane separation [15].

2.4.2 Module Configurations

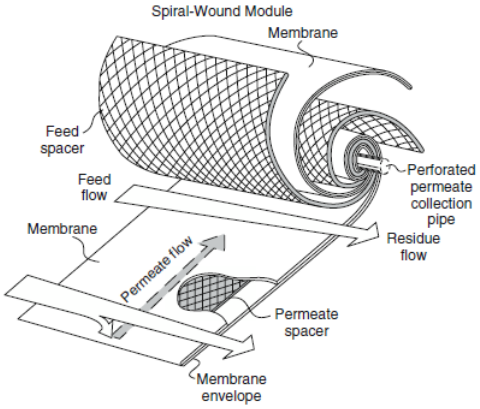
It is important to consider aspects such as the type of separation, risks of plugging of the membranes, packing density, cleaning opportunities and investment costs when it comes to the choice of a membrane configuration. Therefore, a membrane system must be built densely to allow a large membrane surface to be in the smallest possible volume and that is why the membranes are implemented in modules [3]. There are four different types of module designs that are the most important ones: (i) plate-and-frame; (ii) tubular; (iii) spiral-wound; (iv) hollow fiber.



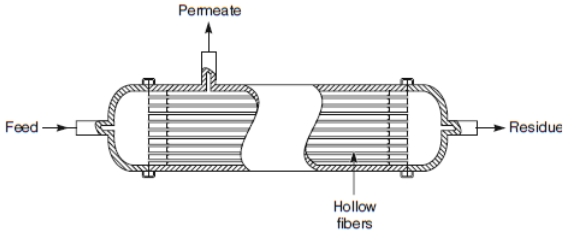
(a) Plate-and-frame.



(b) Tubular.



(c) Spiral-wound.



(d) Hollow fiber.

Figure 8: Schematic representation of module configurations [3].

As previously stated, the here in presented work project aims to test the performance of ceramic membranes, which are implemented only in a tubular module configuration. This type of module consists of a minimum of two tubes: inner tube, which is the membrane tube, and the outer tube, which is the pressure vessel. The module can be made of plastic or metallic materials and it is possible to have more inner tubes depending on the housing structure. he feed stream flows across the length of the membrane tube and is filtered out into the outer shell while retentate is collected at the opposite end of the membrane tube.

One advantages of tubular systems is that they are less prone to fouling than plate-and-frame systems. This configuration also allows to handle feeds with particles, high viscosity feeds. When combining this configuration with ceramic membranes it will be possible the use of harsher chemicals to clean. In contrast to other module configurations, tubular modules have large size which represents a disadvantage. Furthermore, the flow requirements are higher due the large inner diameter of the module which can be an advantage since also feed solutions with bigger particles or fibers can be filtered in contrast to spiral-wound modules.

2.4.3 Membrane Process Parameters

The performance of a membrane filtration process is usually evaluated in terms of the permeate flux, J, and of the membrane separation efficiency, i.e., the retention, R. Both variables depend on the properties of the membrane and the feed, as well as the operating conditions. Ultimately, it is important to consider such phenomena as fouling and concentration polarization, which also have an impact on the membrane performance.

Permeate Flux

The permeate flux, J, stands as the volumetric flow rate of the permeate through the membrane and is usually presented in terms of volume per unit time per unit area ($L\,/m^2h$). As shown in Equation (1), the flux will increase linearly with the transmembrane pressure (ΔP) [6].

$$J = \frac{\Delta P}{R_m \cdot \mu} \tag{1}$$

In the equation above R_m and μ represent the filtration resistance of the membrane and the viscosity of the permeate, respectively. Ideally, only the membrane resistance would affect the permeate flux, but there are several resistances that also must be considered, as shown in Figure 9. The influence of these different resistances is related to the type of membrane and the feed stream properties.

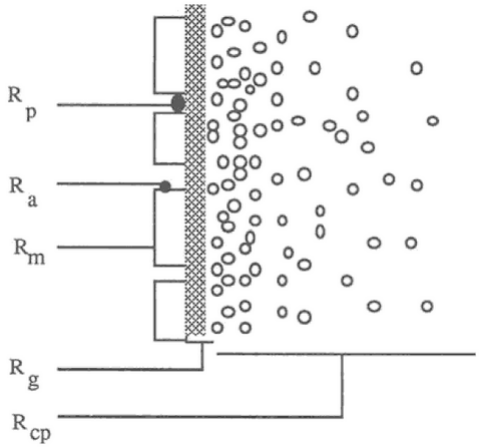


Figure 9: Overview of various types of resistance towards mass transport across a membrane [10]. R_p-Pore block resistance, R_a- Adsorption resistance, R_m- Membrane resistance, R_g- Gel-layer resistance and R_{cp}- Concentration polarization resistance.

Thereafter, it is important to consider the pore block resistance (R_p), the adsorption phenomena resistance (R_a), the resistance associated with the formation of a gel-layer (R_g) and the concentration polarization resistance (R_{cp}) [10]. It is also possible to have filter cake resistance (R_{fc}). Furthermore, the permeate flux can also be influenced by a difference in the osmotic pressure (Π) between the membrane surface and the permeate:

$$J = \frac{\Delta P - \Pi}{(R_m + R_p + R_a + R_{cp} + R_g + R_{fc}) \cdot \mu} \tag{2}$$

The transmembrane pressure is defined as the pressure gradient across the membrane. The pressure on the permeate side,P_{perm}, is often constant and the feed pressure, P_{feed}, is often measured at the inlet of the membrane module. During the process, the flow along the membrane will cause hydraulic pressure losses, which means that the feed pressure at the outlet, P_{ret}, will be lower than at the inlet. Thereby, the ΔP is given as the average transmembrane pressure in the membrane module, as shown in Equation (3) [6].

$$\Delta P = \frac{P_{feed} + P_{ret}}{2} - P_{perm} \tag{3}$$

Retention Coefficients

The retention coefficient represents the extent to which a solute is retained by the membrane. The true retention, R_{true}, is determined accounting for the concentration in the permeate, C_p, and the concentration on the membrane surface, C_m, as shown in Equation (4).

$$R_{true} = 1 - \frac{C_p}{C_m} \tag{4}$$

One of the problems with the determination of this parameter relates to the measurement of the concentration on the membrane surface, which is generally difficult to be performed during operation. Thus, instead of determining the true retention, it is more common to determine the observed retention, R_{obs}, that depends on the bulk concentration, C_b.

$$R_{obs} = 1 - \frac{C_p}{C_b} \tag{5}$$

During the filtration process, a certain solute is retained at the membrane surface to a point when the concentration on the membrane surface, C_m, is greater than the concentration in the bulk solution, C_b. For this reason, the observed retention is always lower than the true retention [10]. Thus, a concentration profile of the membrane surface to the bulk solution will begin to develop, this phenomenon is called the concentration polarization and it will be duly explained in Section 2.5.

Volume Reduction

In some experiments the permeate solution will be continuously removed from the process fluid leading to a reduction of its initial volume, which is expressed by the volume reduction, VR. This parameter is an indicator of how much of the initial feed volume, V_{feed}, has been withdrawn as permeate, V_{perm}:

$$VR = \frac{V_{perm}}{V_{feed}} \tag{6}$$

The volume reduction also points out the extent to which a certain solute has increased in concentration. Therefore, for higher values of volume reduction it is expected that the concentration of a solute or a particle in the retentate is also higher. It is important to note that an increase in solute concentration at the membrane surface will cause a reduction in flux through the membrane to a point where filtration is no longer feasible [17].

2.5 Polarization Phenomena and Membrane Fouling

As stated in Section 2.4.3, it is important to ensure that the membrane process performance is as good as possible. However, during the operation, it is clearly noticeable that the permeate flux, J, tends to decrease over time. The decline of the flux becomes a major problem when it is not possible to reach its initial value even after cleaning, at which point the economic viability of the project is compromised.

The flux decline should be avoided to the maximum, and for this reason, it is necessary to know which are the causes, and consequently, the measures that must be taken to avoid it. The concentration polarization phenomenon and the membrane fouling are the major cause of this problem, and they will be the focus of this chapter that aims to provide a detailed explanation of both.

Concentration Polarization

During membrane filtration, the solute particles in the feed solution are conveyed to the membrane surface by convective transport (J_v), and some of these particles will be retained on the surface of the membrane while the other particles will pass through the membrane [6]. The retained solute particles will start to accumulate on the membrane and forming a solute buildup that is known as concentration polarization, and it will generate a diffusive flow back to the feed bulk [10]. This phenomena is described in Figure 10.

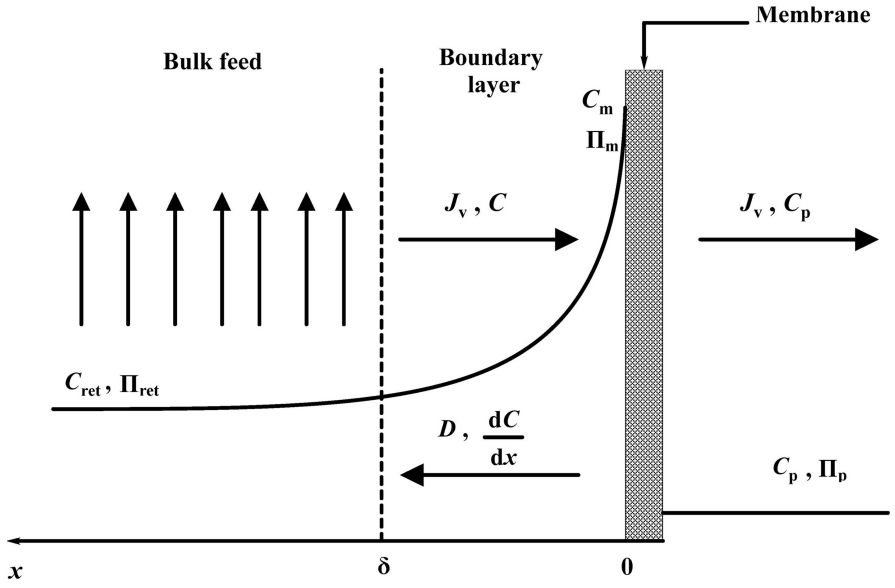


Figure 10: Schematic representation of concentration polarization during membrane filtration. Adapted from [10].

The quantification of the concentration polarization phenomenon can be explained by the mass transfer model that is briefly described downwards.

- **Mass Transfer Model**

At steady conditions the convective transport of solute to the membrane is equal to the sum of the amount of solute passing with the permeate plus the diffusive back transport of the solute as described by Equation 7.

$$J_v \cdot C + D \cdot \frac{dC}{dx} = J_{C_p} \tag{7}$$

In order to integrate Equation 7, the boundary conditions described in Equation 8 were applied resulting in Equation 9.

$$\left\{ \begin{matrix} x = 0 \rightarrow C = C_m \\ x = \delta \rightarrow C = C_b \end{matrix} \right\} \tag{8}$$

$$ln\left(\frac{C_m - C_p}{C_b - C_p}\right) = \frac{J_v \cdot \delta}{D} \tag{9}$$

The mass transfer coefficient (k) is the ratio of the diffusion coefficient (D) and the thickness of the boundary layer (δ), as shown by Equation 10. The rearrangement of Equation 9 will become the general equation for the concentration polarization, Equation 11.

$$k = \frac{D}{\delta} \tag{10}$$

$$\frac{C_m - C_p}{C_b - C_p} = exp\left(\frac{J_v}{k}\right) \tag{11}$$

Membrane Fouling

Fouling can be described as a decline in flux with time of operation while all operating parameters, such as pressure, flow-rate, temperature, and feed concentration are kept constant [6]. The flux decay will depend on the system but is usually rapid in the first few minutes, followed by a more gradual decline [6]. This behavior differs from that observed when it comes to concentration polarization phenomena, in which the decrease of the flux tends to be constant after some time, as described in Figure 11 [10].

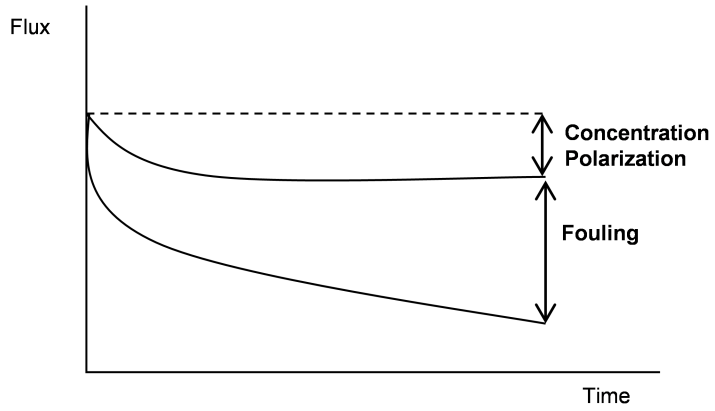
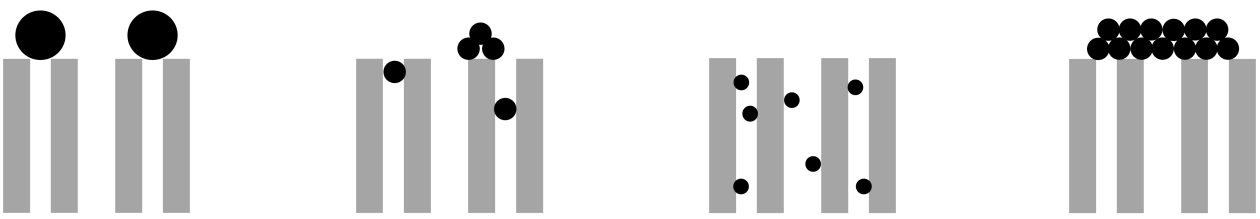


Figure 11: Flux decline for concentration polarization and fouling phenomenon. Adapted from [10].

In general, it is possible to divide membrane fouling into four major types: (i) organic; (ii) inorganic, (iii) colloidal and (iv) biological. Each of these fouling types is caused by different foulants and fouling mechanisms, and they can often occur simultaneously. Organic fouling is caused by organic macromolecules (i.e., humic acids) and biopolymers (i.e, proteins and polysaccharides) and it has four different mechanisms of formation: complete pore blocking, intermediate blocking, standard blocking and cake-layer formation (Figure 12) [8] [22]. Inorganic fouling is the result of the deposition and subsequent crystallization of soluble salts (i.e., calcium and silica salts) on the membrane surface leading to the formation of a cake-layer [22]. Colloidal fouling is caused by deposition of fine particles with sizes ranging from 1 to 1000 nm [5], which it will also form a cake-layer. Finally, biological fouling occurs due to the deposition, accumulation, growth and metabolism of microorganisms on a membrane surface also causing cake-layer formation [22].



(a) Complete pore blocking. (b) Intermediate blocking. (c) Standard blocking. (d) Cake-layer formation.

Figure 12: Mechanisms of organic fouling formation. Adapted from [22].

- **Consequences of fouling and how to avoid it**

Membrane fouling can cause a decrease of the effectiveness of the separation process by reducing the flux, increasing the filtration resistance, changing the selectivity of the membrane, and increasing the energy demand [19]. All this may undermine the economic viability of the process. For all those reasons it is important to avoid/reduce the fouling of the membrane that can be caused by different foulants and fouling mechanisms. Therefore, it is necessary to consider different techniques to reduce fouling depending on the separation being carried out. Overall, there are four main methods to avoid/reduce fouling on a membrane system:

1. Pretreatment of the feed solution - Finding an appropriate pretreatment for the feed solution is the first step to prevent fouling of the membrane. According to the type of feed solution, different pretreatments may be used, such as heat treatment, pH adjustment, addition of a complexing agent, pre-microfiltration [10];
2. Membrane properties - Choosing a membrane with certain properties is highly important. For instance, a porous membrane is more susceptible to fouling than a dense membrane. The pore size and membrane material should also be taken into account [10];
3. Module and process conditions - Some module configurations are more prone to fouling than others, which is an important aspect to consider when it comes to choosing one. Furthermore, different operating conditions will affect the fouling of the membrane such as temperature, cross-flow velocity, pressure [10];
4. Membrane cleaning - Although all the previous methods contribute to avoid and reduce fouling, the cleaning step is always performed. The choice of the cleaning agent, the cleaning method and cleaning frequency will depend upon the separation system [10].

3 Materials and Methods

3.1 Molasses and Sugar Solutions

The beet molasses were the main product under study in this project and were supplied by *Nordic Sugar*, Örtofta, Sweden. In Section 3.5 all analytical methods that were performed to determine the characteristics of molasses are described and the results of these tests are shown later in Tables 5 and 6.

Different model sugar solutions were prepared to be tested in the membrane screening step that is described in Section 3.4.2. The composition of these solutions is presented in Table 3.

Table 3: Composition in %wt of the solutions prepared during the studies.

Solution/Compostion	Sucrose	Glucose	Fructose
Solution A	0.5%	-	-
Solution B	-	0.5%	-
Solution C	-	-	0.5%
Solution D	0.5%		
	0.49%	0.05%	0.05%

According to the company that supplied the sugar beet molasses, the sugar content on them was around 0.5-10%wt. For that reason, it was decided that all the solutions should have a concentration of 0.5%wt of sugars. The filtration of Solution D aimed to reproduce the filtration of a molasses solution. Considering the information given in [12], sucrose represents 98% of the sugar content in the sugar beet molasses and 2% is glucose and fructose. Thus, Solution D has the same sugar composition.

3.2 Membranes and Module

The aim of the project is to study the performance of different tubular ceramic nanofiltration membranes. Table 4 gives the information regarding the characteristics of each tested membrane.

Table 4: Properties of the tested membranes.

Membrane	MWCO (Da)	Material & Substrate	L (mm)	D (mm)	Membrane Area (m^2)
LC1	200	$\alpha - Al_2O_3$	250	7	0.055
LC2	350				

Figure 13: Membranes LC1 and LC2.

All the experiments for the different membranes were performed in the same tubular module, shown in Figure 14. Further detailed information about the module features can be found in Appendix A.

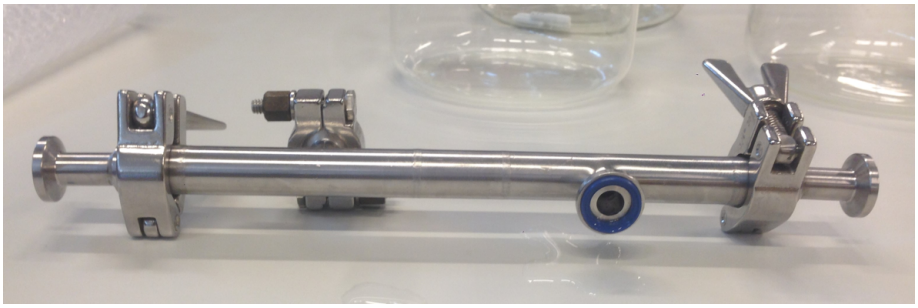


Figure 14: Tubular Module.

3.3 Equipments

The experimental set-up used for the parametric studies is shown in Figure 15, and it should be noted that the permeate and retentate were recycled to the feed tank. The experimental apparatus consisted of a 15 L feed tank where the experimental solutions were heated by an electric heater. Inside the tank, two Pt-100 temperature sensors (Pentronic, Gunnebo, Sweden) were placed and connected to a temperature controller, one to control the temperature in the tank and the other to record the temperature. Transmembrane pressure was regulated by two manual valves, one on the retentate side and the other on the permeate side. Three pressuremeters (Trafag DCS40.0AR, Regal Components AB, Uppsala, Sweden) were place at the inlet, the permeate outlet and retentate outlet. The permeate flow was measured with an electronic balance (PL6001-S, Mettler-Toledo Inc., Columbus, USA.). A displacement pump (Hydra-cell D25XL, Wanner, Minneapolis, MN, USA), connected to a frequency converter (ELEX 4000, Bergkvist & Co., AB, Gothenburg, Sweden), was used to control the cross-flow velocity. The pressure indicators, the temperature transmitters, the flowmeter, and the balance were connected to a computer and all the data were recorded using the LabVIEW® 2009 software (National Instruments Co, Austin, TX, USA).

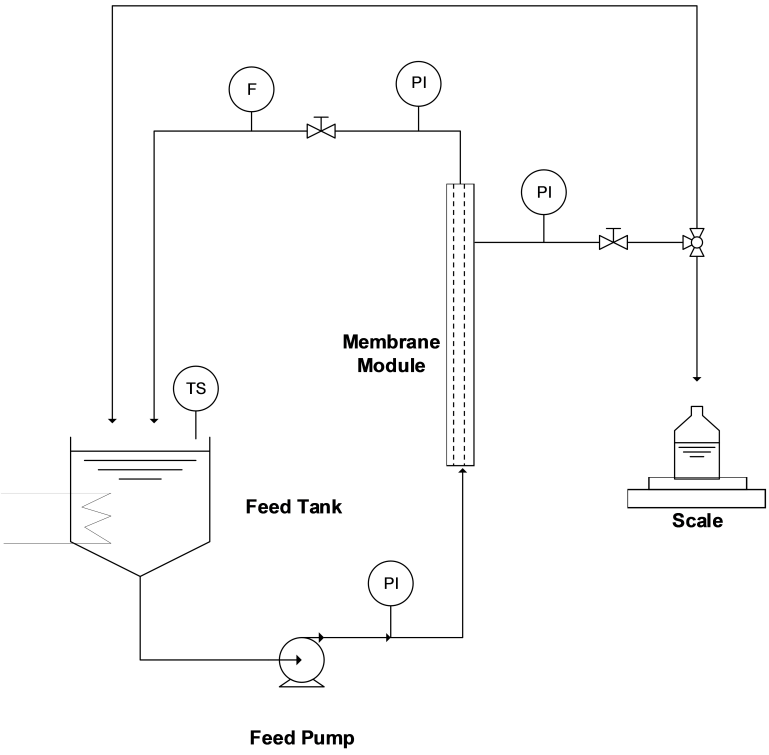


Figure 15: Schematic representation of the experimental set-up.

3.4 Operating Procedures

After a brief presentation on the membranes, the module and all the equipment that is required for the experimental set-up, it is essential to provide a detailed explanation of all the procedures performed during this project.

Thus, this section will focus on describing not only test procedures, but also on secondary procedures such as membrane cleaning and PWF measurement, which are also essential for obtaining reliable results.

3.4.1 Membrane Cleaning and PWF Measurement

The membrane cleaning is a key step when it comes to membrane processes and should be as efficient as possible. For this reason, it is important to select the most efficient cleaning agent and the operating conditions that will allow the best/most efficient performance of each membrane.

The membrane LC1 was cleaned with an alkaline cleaning agent, P3-Ultrasil 110 (Ecolab AB, Älvsjö, Sweden), and an acidic cleaning agent, P3-Ultrasil 73 (Ecolab AB, Älvsjö, Sweden). The membrane was first cleaned with the alkaline solution, followed by the acidic solution and finally again with the alkaline solution, each for 1 h. For the Membrane LC2, it was necessary the use a stronger acidic cleaning agent, P3-Ultrasil 75 (Ecolab AB, Älvsjö, Sweden).

The cleaning of both membranes was performed at 50°C, with a TMP of 3 bar and a CFV of 3 m/s. The cleaning agent was used with a concentration of 0.5%wt and with a volume of 13 L. In the end of each cleaning step, the membrane was rinsed with deionized water to ensure the removal of any traces of cleaning agent.

The PWF was initially measured before carrying out any experiment with the new membranes (J_{wi}). After performing each experiment, the PWF of the fouled membrane (J_{w*}) was again measured in order to assess the membrane fouling. Hereafter, the membrane was cleaned according to the procedure above mentioned and the PWF of the cleaned membrane (J_w) was one last time measured to ensure that the cleaning was effective. The measurement was carried out at 30°C and with a CFV of 3 m/s, for a TMP range from 1 to 9 bar with a step size of 2 bar. The PWF was measured for 5 min at each pressure.

3.4.2 Membrane Screening

The membrane screening consisted of carrying out parametric studies with each membrane, leading to the conclusion of the most promising membrane to the desired separation.

Primarily, both membranes were tested with solutions A, B and C, in order to verify how the membrane behaves when it comes to the separation of single sugars. Afterwards, Solution D was tested, this specific solution aims to reproduce the composition of sugars of a molasses solution. The composition of each solution is provided in Table 3.

Parametric Studies

The parametric studies allow the assessment of the influence of the operating conditions on the permeate flux and on the retention levels. These tests were performed at 70°C, with a CFV of 1 m/s and 3 m/s, at TMP of 2, 5 and 10 bar and both the retentate and the permeate were recycled to the feed in order to maintain a constant concentration.

The tests were always started on the highest CFV and the lowest TMP, the TMP was then increased to the highest value. After this, the new velocity was set and the TMP was decreased back to the lowest value. This procedure helps to minimize the risk of cake formation on the membrane surface and, in addition, the membrane fouling.

All the measurements were carried out for 15 min at each operating conditions and samples of the permeate were collected for each pressure. The composition of the samples was subsequently analysed and the retention evaluated.

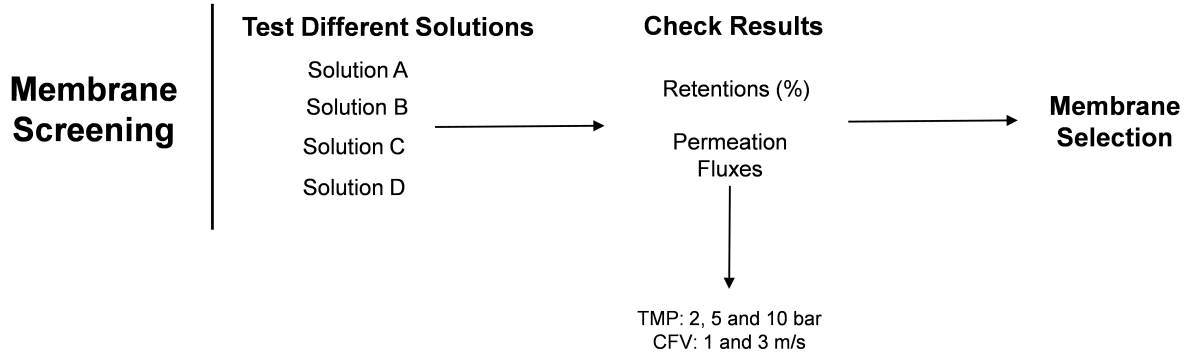


Figure 16: Schematic representation of the membrane screening stage.

3.4.3 Membrane Performance

After the membrane screening was done, it was possible to conclude that Membrane LC1 is the most suitable to achieve the desired separation. Hereupon, tests to check the performance of this membrane at different temperatures were carried out.

In order to assess on the effect of temperature on the flux and retention, the same parametric studies were performed at 60°C and 80°C. These tests were only performed for Solution A. These last test, together with those performed in the screening phase at 70°C , will lead to the conclusion about the best operating conditions to achieve the best possible results.

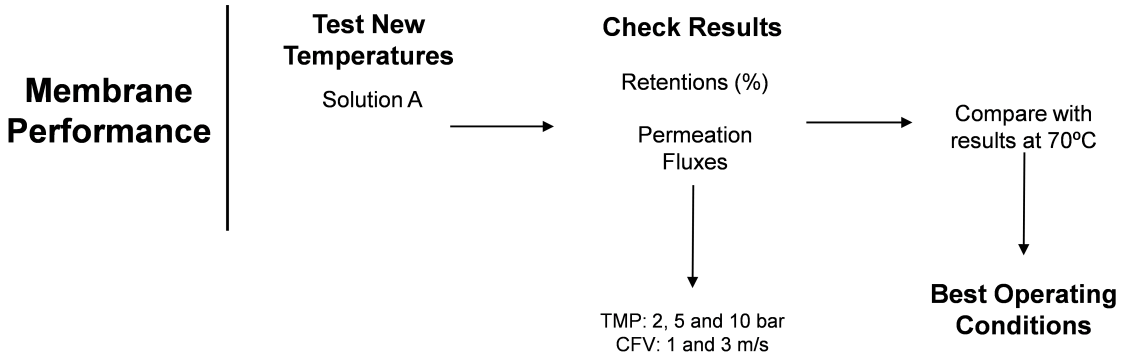


Figure 17: Schematic representation of the membrane performance stage.

3.5 Analytical Methods

3.5.1 Total Solids and Ash

To determine the total solids (TS) content, three samples with approximately 10 mL of molasses were dried in an oven at 105°C for 72 h and then cooled to room temperature for 1 h in a desiccator. Then, the weight of the samples was measured.

The dry samples were then moved to a furnace, where they were first heated to 105 °C for 30 min. Immediately after, they were again heated to 250°C at a heating rate of 5°C/min and this temperature was maintained for 30 min. Finally, the temperature was raised to 575°C at a heating rate of 10°C/min and it was held for 3 h. The ash content was calculated from the weight of the remaining samples after cooling to room temperature in a desiccator for 1 h.

3.5.2 Lactic Acid

The molasses samples were first acidified to a pH of 5 by using 95% sulphuric acid, then diluted 20 times and filtered with a 0.2 μm filter (Scheicher & Schuell, Germany). The samples were analysed by high-performance liquid chromatography (HPLC) using a Shimadzu HPLC system (Shimadzu Corp., Kyoto, Japan) which was equipped with an RID-10A refractive index detector (Shimadzu Corp., Kyoto, Japan).

3.5.3 Density, Conductivity and pH

The conductivity of the molasses was measured using an HI 99301 EC/TDS meter equipped with an HI 76306 probe (Hanna Instruments Inc., Woonsocket, RI, USA.)

The pH of the molasses was determined using an InLab Expert pH (Mettler, Toledo.)

The density of the molasses was determined using an analytical hydrometer (Kebo Grave, Spånga, Sweden).

3.5.4 Sugar Content

The molasses samples were first filtered using a 0.2 μm filter (Scheicher & Schuell, Germany) and then diluted. The sugar content was determined through high-performance anion exchange chromatography coupled with pulsed amperometric detection (HPAE-PAD), using for that a ICS-3000 chromatography system (Dionex Corp., USA). The system was equipped with a Carbo Pac PA1 analytical column, a ICS-3000 SP gradient pump and an AS-AP autosampler. The eluents used were: (1) dionized water; (2) sodium hydroxide, 200 mmol/L; (3) sodium hydroxide, 200 mmol/L and sodium acetate, 170 mmol/L. The flow-rate was 1 mL/min. The standards used were D-sucrose, D-glucose, D-fructose and D-raffinose.

3.5.5 Molecular Mass Distribution

The molecular mass distribution of molasses was determined by size-exclusion chromatography (SEC) using a Waters 600E chromatography system (Waters, USA). The system was equipped with a refractive index (RI) detector (model 2414, Waters) and UV detector (model 486, Waters). The analytical column was packed with 30 cm Superdex30 and 30 cm Superdex200 (GE Healthcare, Sweden). The injection volume was 500 μm and a solution of 0.5 wt% NaOH was used as eluent at a flow-rate of 1 mL/min. The system was calibrated with polyethylene glycol standards with peak molecular masses of 0.4, 4, 10 and 35 kDa (Merck Schuchardt OHG, Germany.) Before performing the test, all samples were filtered using a 0.2 μm filter (Scheicher & Schuell, Germany).

4 Results and Discussion

4.1 Molasses Characterization

The analysis methods performed with the molasses samples were described in the previous section and the results related with the first three tests are exposed in Table 5.

Table 5: Molasses characteristics.

pH	7.14
Conductivity (mS/cm)	1.19
ρ (g/cm^3)	1.852
TS (%)	70.6 $\pm$ 6.1
Ash (%)	22.7 $\pm$ 0.5
Lactic Acid (g/L)	2.5 $\pm$ 0.1

Sugar Content

The sugar content of the molasses is shown in Table 6 and discussed shortly after.

Table 6: Molasses sugar content.

Sugar Content (mg/g of molasses)	
Sucrose	470
Glucose	<1
Fructose	<1
Raffinose	10

According to [12], it would be expected that the sugar in molasses were 98% composed of sucrose, the remainder being mainly glucose and fructose and some trace amounts of raffinose, yet the obtained results showed that in the tested sample, the raffinose concentration was higher than the glucose and fructose.

The deviation of results to [12] is probably related with two factors: (i) place of cultivation and (ii) sugar extraction method. Molasses under study in [12] were produced in Germany, while the ones tested in this project were produced in Sweden. Different cultivation sites suggest different soil properties, climate, and then beets with different sugar content and sugar composition. It is also necessary to consider that, being produced in different places, the method to extract the sugars from the beets can also be different, which it will influence the properties of its by-products, including the molasses.

As explained before, the composition in sugars of Solution D was decide according with information provided in [12]. The aim was to have a solution with the same sugar composition of sugar beet molasses but, at that point, the composition of the molasses that were provided by *Nordic Sugar* was unknown. Considering the difference in sugar composition of the Solution D and the molasses, the results obtained when performing experiments with Solution D will not be as informative as expected.

Molecular Mass Distribution

The molecular mass distribution of the molasses was measured by SEC following the procedure described in Section 3.5. The SEC diagram presented in Figure 18 shows the molecular mass distribution of the molasses sample and a sugar standard. [1]

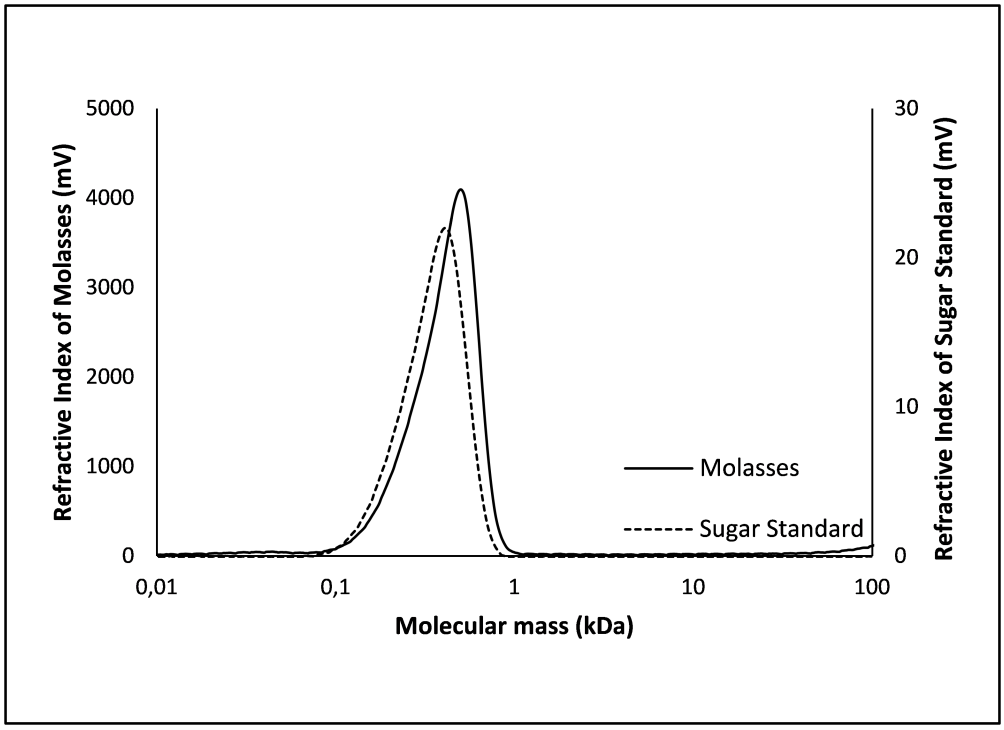


Figure 18: Molecular mass distribution of molasses and sugar standard (measured as refractive index).

From the RI curve it can be seen that both samples contained a high amount of the same material, around 0.5 kDa. This component was most certainly sucrose, which has a molecular mass of 0.34 Da. The SEC results corroborate the results obtained by high-performance anion exchange chromatography (Table 6), where has been shown that sucrose was the main component in the molasses sample.

Figure 19 shows the UV response of the molasses where several peaks of high molecular mass (100-10000 kDa) can be seen, consisting of colloidal particles.

[1] For the sugar content test, five different sugar standards were prepared. These standards were composed of equal amounts of sucrose, glucose, fructose and raffinose and each of them had a different concentration.

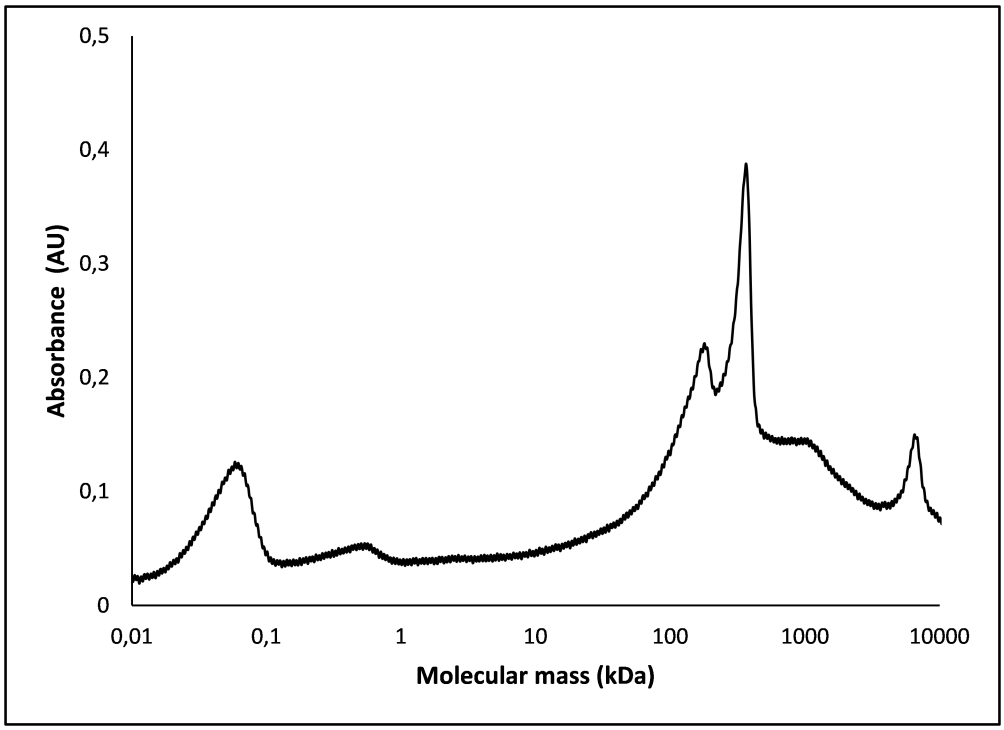


Figure 19: Molecular mass distribution of molasses (measured as UV absorbance).

4.2 Pure Water Flux and Hydraulic Permeability

The determination of the pure water flux of the membrane, J_{wi}, is very important insofar as it will be a reference to assess the membrane fouling after the experiments. Furthermore, it will also allow to evaluate the efficiency of the cleaning procedure. The procedure regarding the PWF measurement and the membrane cleaning was explained in Section 3.4.1. The influence of TMP on the pure water flux of each tested membrane is shown in Figure 20. Detailed data related to the pure water flux can be found in Appendix C.

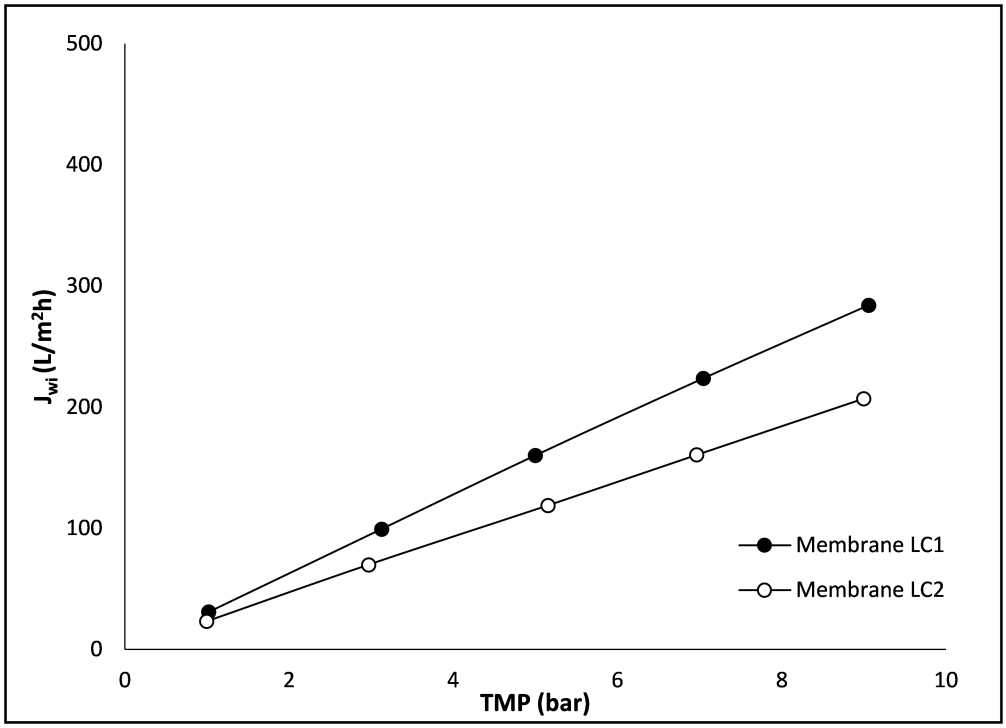


Figure 20: Influence of TMP on the pure water flux, J_w, for each membrane. T=30°C and CFV=3 m/s.

Hydraulic permeability, L_p, represents the permeation capacity of a membrane, allowing the comparison of different membranes. This parameter is the slop of Equation (12) and describes the linear variation of the pure water flux (J_{wi}) as a function of TMP.

$$J_{wi} = L_p \cdot TMP \tag{12}$$

It is important to consider that different temperatures were used throughout the experiments, and in order to discuss the obtained results, the hydraulic permeability should be rectified to a standard temperature of 25°C. The correlation (13) takes into account the effect of temperature on the viscosity of the water which will affect the flux and membrane permeability.

$$L_{p\,25^{\circ}C} = \left(\frac{L_p}{0.901}\right) \cdot exp^{\left(-6.96+\frac{2044}{273.15+T}\right)} \tag{13}$$

Where L_p is the hydraulic permeability measured at certain temperature T in °C. Hydraulic permeability values along with their correction to 25°C are given in Table 7.

Table 7: Hydraulic Permeability (L_p) of tested membranes.

Membrane	**Linear Regression**	$\mathbf{L_p\ (L/hm^2bar)}$	$\mathbf{L_{p\,25^{\circ}C}\ (L/hm^2bar)}$
LC1	$J_{wi} = 31.6 \cdot TMP$ $R^2 = 0.9997$	31.6	28.2
LC2	$J_{wi} = 22.9 \cdot TMP$ $R^2 = 0.9999$	22.9	20.5

The results presented above indicate that Membrane LC1 had the highest hydraulic permeability, which was not expected due to its low MWCO, 200 Da. It is expected that membranes with lower MWCO have tighter pores that hinder the transport of water through the membrane, resulting in a decrease of their L_p. Nevertheless, a theoretical clarification for this result can be found explained below. Considering the absence of fouling when measuring the PWF, and assuming that the capillary pores in the membrane is uniform, it is possible to use the Hagen-Pouseuille equation to estimate the pure water flux.

$$J_{wi} = \frac{\varepsilon \cdot r_p^2}{8\eta \cdot \tau} \cdot \frac{TMP}{l_p} \tag{14}$$

Where ε is the membrane porosity, η is the dynamic viscosity of the water, τ is the tortuosity factor, r_p is the pore radius and l_p is the membrane thickness. The combination of Equations (12) and (14) gives an expression that theoretically describes the hydraulic permeability:

$$L_p = \frac{\varepsilon \cdot r_p^2}{8\eta \cdot \tau \cdot l_p} \tag{15}$$

According to Equation (15), the high permeability of Membrane LC1 may be explained by certain parameters that are related to the membrane itself.

4.3 Membrane Screening

4.3.1 Permeate Fluxes

The permeate fluxes were measured during the parametric studies, that aim to evaluate the influence of TMP and CFV on them, and were held for Membranes LC1 and LC2 following the procedure described in Section 3.4.2. For a better follow-up of the results and their discussion, this section is divided into three parts: (i) Membrane LC1, (ii) Membrane LC2 and (iii) Membrane LC1 vs Membrane LC2. Detailed data related to the permeate fluxes of Membranes LC1 and LC2 can be found in Appendix D.1.

Membrane LC1

The effect of TMP and CFV on the permeate fluxes of each tested solution, when using Membrane LC1, is presented in Figure 21.

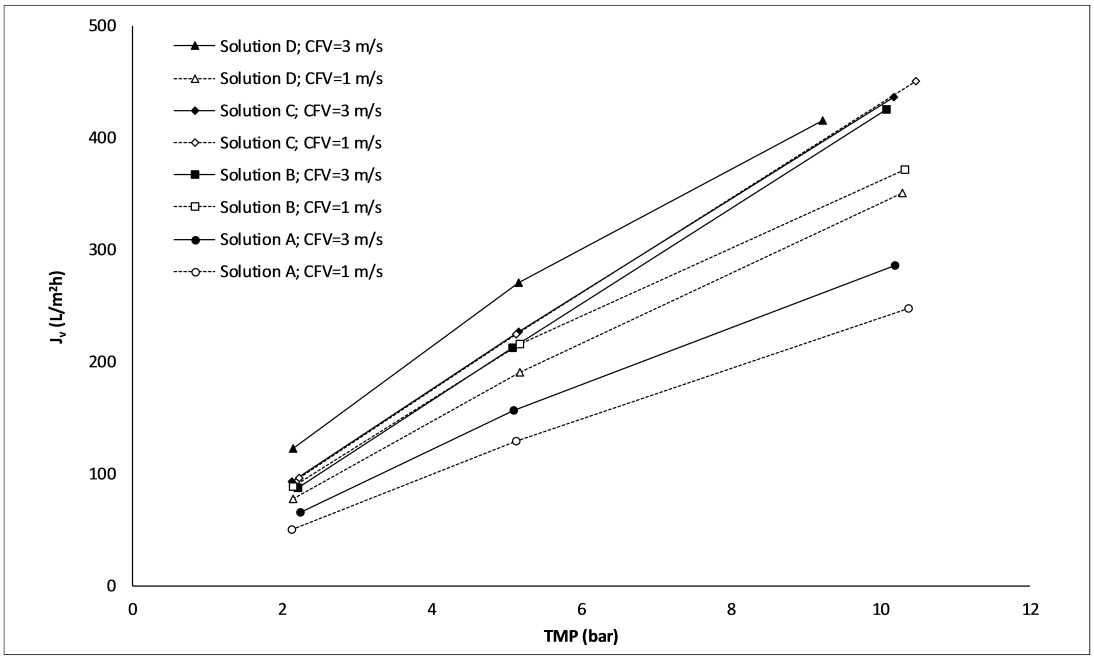


Figure 21: Influence of TMP and CFV on the permeate fluxes of tested solutions using the Membrane LC1. T=70°C.

Figure 19 shows that the permeate fluxes of all tested solutions increased with increasing TMP. The permeate fluxes of Solution A were considerably lower than those of the other solutions. As shown in Table 5, Solution A is composed only of sucrose which has a higher MW (342.3 Da) than glucose and fructose (180.2 Da) and this value is close to the membrane MWCO (200 Da), which may indicate that the membrane was retaining the sucrose as desired. Moreover, the permeate fluxes of Solution A were higher at a CFV of 3 m/s, as expected.

For Solution B, the permeate fluxes were similar at lower pressures. The results show that CFV did not influenced glucose permeation to lower TMP values but may had a heavier impact on fluxes when performing the experiments at a TMP close to 10 bar.

The permeate fluxes of Solution C were very similar for both CFVs, which indicates that the permeation of fructose was not influenced by this parameter. Furthermore, it is noticeable that Solutions B and C had similar results which it is related to their close molecular weight.

The permeate fluxes of Solution D were lower than for Solutions B and C and higher than for Solution A, when operating at a CFV of 1 m/s. Since Solution D is composed of sucrose (98%) and glucose and fructose (2%), it was expected that the membrane had been retaining sucrose, but not as much as in Solution A which is composed only of sucrose. For a CFV of 3 m/s, Solution D had the highest permeate fluxes which was not in line with the previous results.

Membrane LC2

The obtained results of the parametric studies for all tested solutions using Membrane LC2 are shown in Figure 22. It is possible to consult all the detailed data in Table 11, Section D.1.

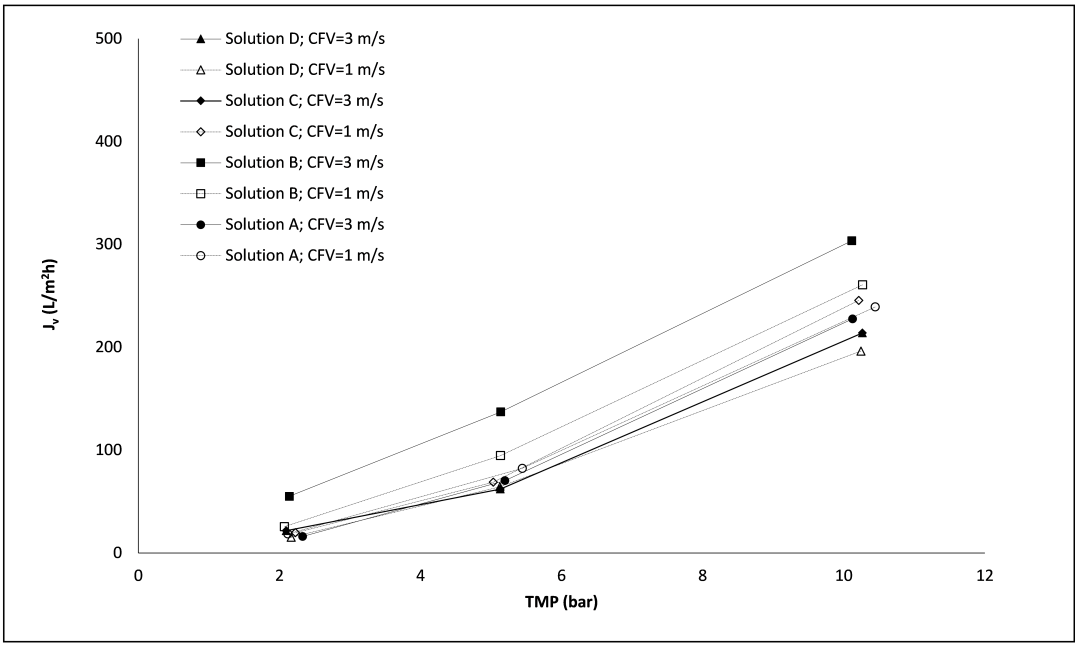


Figure 22: Influence of TMP and CFV on the permeate fluxes of tested solutions using the Membrane LC2. T=70°C.

Figure 22 shows that the TMP enhanced the permeate fluxes of all solutions. The permeate fluxes of Solution A were not influenced by CFV. Besides this, the permeate fluxes of Solution A were lower than for Solutions B and C, which denotes that the membrane was probably retaining sucrose, even though the Membrane LC2 has a higher MWCO (350 Da) than the MW (342.3 Da) of sucrose molecules.

Regarding Solution B, the permeate fluxes increased with CFV and were higher than those of Solution A, which means that the membrane was permeating glucose molecules.

For Solution C, the permeate fluxes were higher at 1 m/s, as opposed to what was expected. As explained in section 3.4.2, the parametric tests were started at the highest CFV and then decreased to the lowest CFV, so it is possible that the membrane has been fouled during the first part thereby affecting the fructose permeation by the membrane when the lower CFV was tested.

Finally, the permeate fluxes of Solution D increased with CFV and were lower than for the other solutions, suggesting that the membrane may have been retaining some sucrose molecules as desired.

Membrane LC1 vs Membrane LC2

In order to compare directly the results for both membranes, the permeate fluxes were plotted according to the CFV used. In Figures 23 and 24 it is presented the results for Membrane LC1 and Membrane LC2 at CFV of 3 m/s and 1 m/s, respectively.

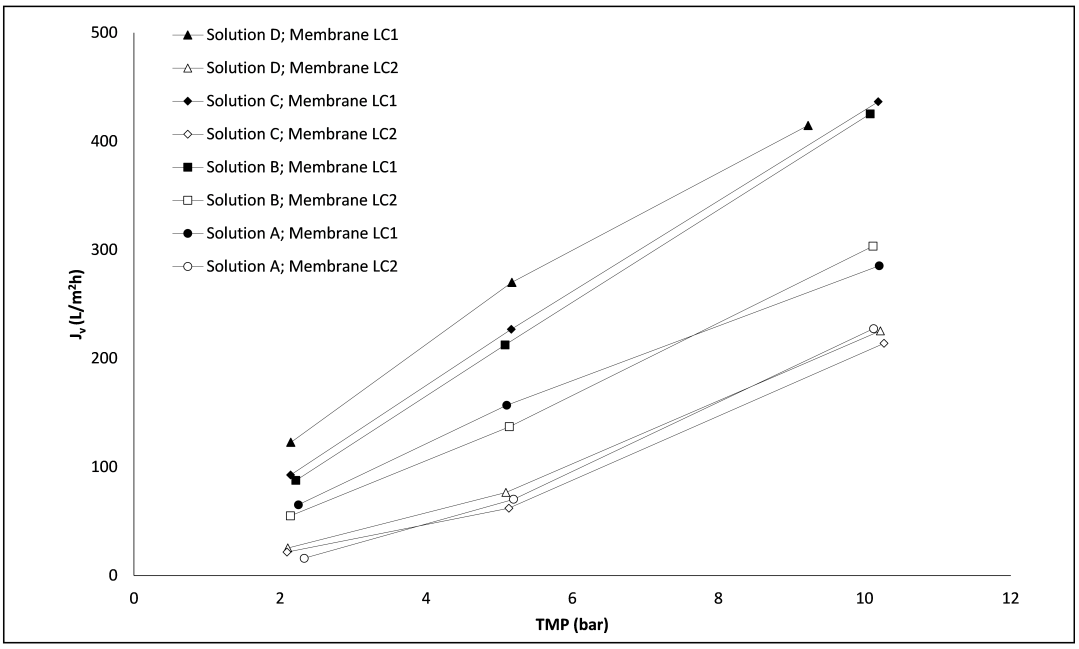


Figure 23: Comparison of permeate fluxes of Membranes LC1 and LC2. CFV=3 m/s.

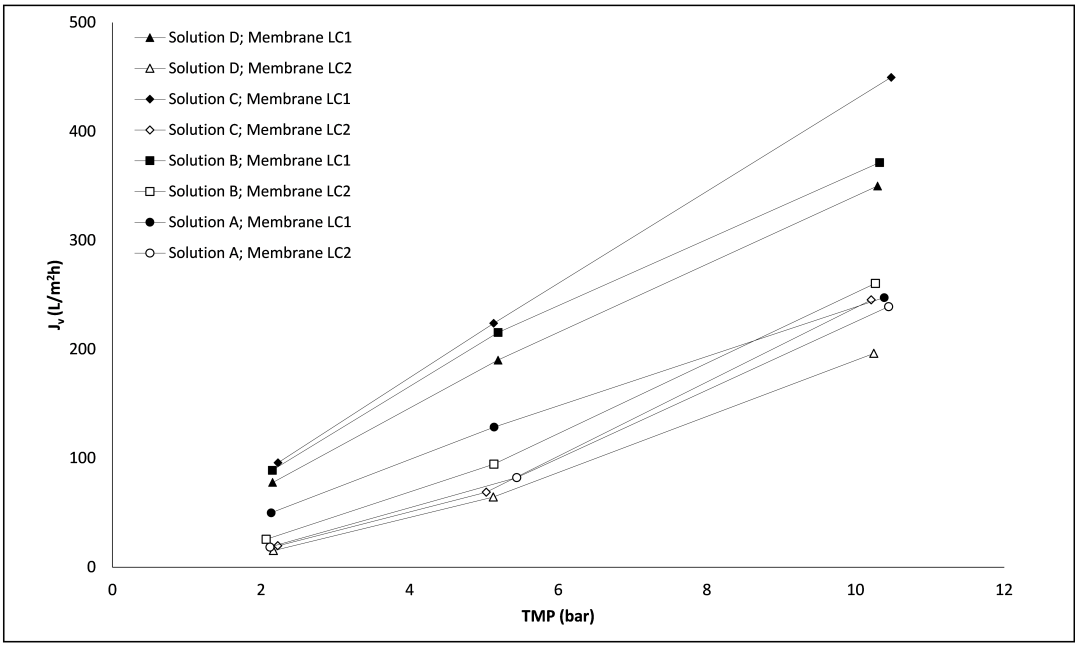


Figure 24: Comparison of permeate fluxes of Membranes LC1 and LC2. CFV=1 m/s.

Figures 23 and 24 show that the Membrane LC1 provided higher permeate fluxes for both CFVs. The results are in accordance with what it was verified in Section 4.2, Membrane LC1 has a higher hydraulic permeability than Membrane LC2, and thus it will give higher permeate fluxes.

Overall, it is expected that Membrane LC1 was retaining more sucrose molecules than Membrane LC2 but these can only be confirmed by the analysing the sugar content of each permeate sample taken during the parametric studies. The retention results are presented in the next section.

4.3.2 Retention Levels

The retention level provides information regarding the amount of solute being retained by the membrane, thus providing valuable information on the performance of the membrane. As described in Section 3.4.2, samples were collected during the parametric studies for further analysis of their sugar content and determination of the retention levels of the components of each solution tested. To a better follow-up of the results and their discussion, this section is divided into two parts: (i) Membranes LC1 and LC2 and (ii) Solution A vs Solution D. Detailed data related to the retention levels can be found in Appendix D.2.

Membranes LC1 and LC2

Figures 25 and 26 show the retention of sugar when filtering solutions A, B and C by Membranes LC1 at CFVs of 1 and 3 m/s. Before analysing the results, it is important to remember that solutions A, B and C are composed of sucrose, glucose and fructose, respectively. Thus, the results presented in those figures are related only to these compounds.

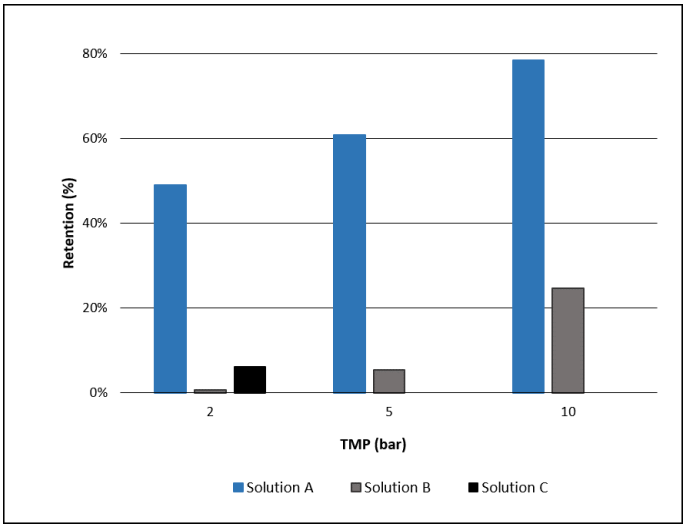


Figure 25: Influence of TMP and CFV on retention of components of solutions A, B and C using Membrane LC1 (200 Da) during the parametric studies. CFV=1 m/s.

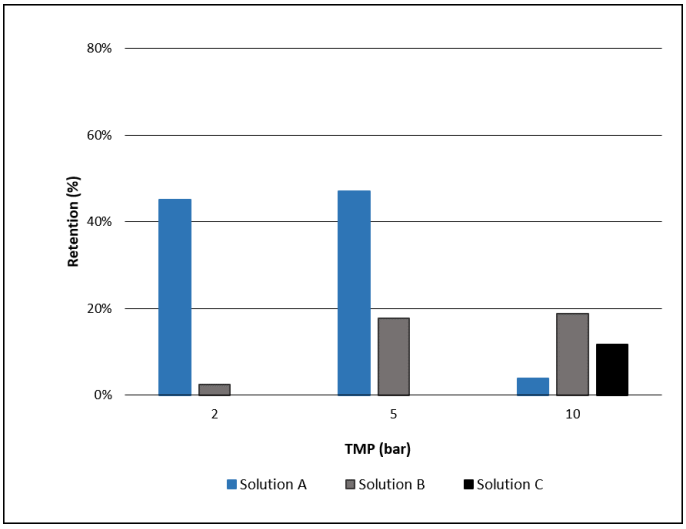


Figure 26: Influence of TMP and CFV on retention of components of solutions A, B and C using Membrane LC1 (200 Da) during the parametric studies. CFV=3 m/s.

Regarding Membrane LC1, Figure 25 shows an increase in retention with increasing TMP for both Solutions A and B, while retention of Solution C was approximately zero. This may be caused by the concentration polarization phenomenon that explains the increase in solute concentration at the membrane surface and therefore a higher resistance to permeation of molecules of Solutions A and B. In addition, the retention of Solution A was always greater than the retention of Solutions B and C, which was probably due to the fact that the MW of the sucrose molecules is higher than the MWCO of the membrane.

When operating at a CFV of 3 m/s (Figure 26), it was seen the opposite effect on the retention of Solution A, while the results for the other solutions remained similar. The decrease of the retention of Solution A was due to the increase of the CFV during the tests, forcing the passage of the molecules through the pores of the membrane.

Figures 27 and 28 show the retention of sugar when filtering solutions A, B and C by Membranes LC2 at CFVs of 1 and 3 m/s. Once again, before analysing the results, it is important to remember that solutions A, B and C are composed of sucrose, glucose and fructose, respectively. Thus, the results presented in those figures are related only to these compounds.

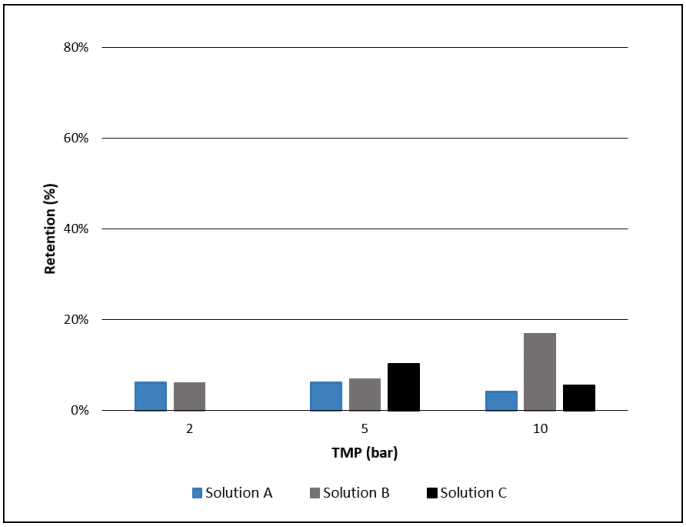


Figure 27: Influence of TMP and CFV on retention of components of solutions A, B and C using Membrane LC2 (350 Da) during the parametric studies. CFV=1 m/s.

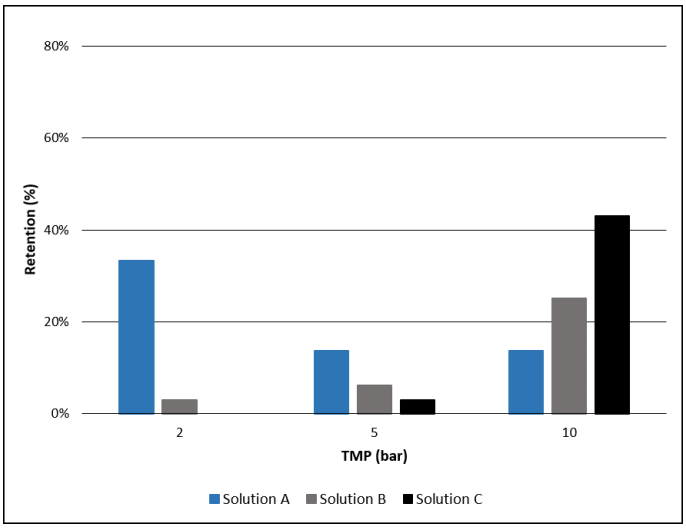


Figure 28: Influence of TMP and CFV on retention of components of solutions A, B and C using Membrane LC2 (350 Da) during the parametric studies. CFV=3 m/s.

Regarding Membrane LC2, Figure 27 shows that the retention of all solutions was very low. The current results were expected for Solutions B and C, due to their low MW compared to MWCO of the membrane but not for Solution A that presents a MW quite similar to the membrane MWCO. Thus, a higher retention of Solution A would be expected.

When operating at a CFV of 3 m/s (Figure 28), the retention of all solutions was higher. Solution A had a decrease in retention levels with increasing TMP while Solutions B and C had not. For Solution C at 10 bar, the retention level was higher than for Solution A, which is highly unlikely to occur and it has no theoretical explanation. However, this particular result may be due to a high fouling of the membrane resulting in blockage of the pores and consequent retention of fructose molecules.

Finally, it can be concluded that Membrane LC1 provided better results: high sucrose retention (Solution A) and low retention of glucose and fructose (Solutions B and C). These results indicate that the Membrane LC1 is most appropriate to achieve the retention of sucrose through membrane filtration.

Solution A vs Solution D

This section aims a direct comparison between the retention of sucrose in Solution A and Solution D, presented in Figure 29 and 30 for Membranes LC1 and LC2, respectively. The goal is to understand how the membrane behaves when filtrating sucrose molecules in a single sugar solution (Solution A) and in a mixture sugar solution (Solution D), i.e., how the presence of other sugars in solution, such as glucose and fructose, influences the permeation of sucrose. Hence, it will be possible to take some conclusions about what to expected when performing the same experiments with a solution of sugar beet molasses.

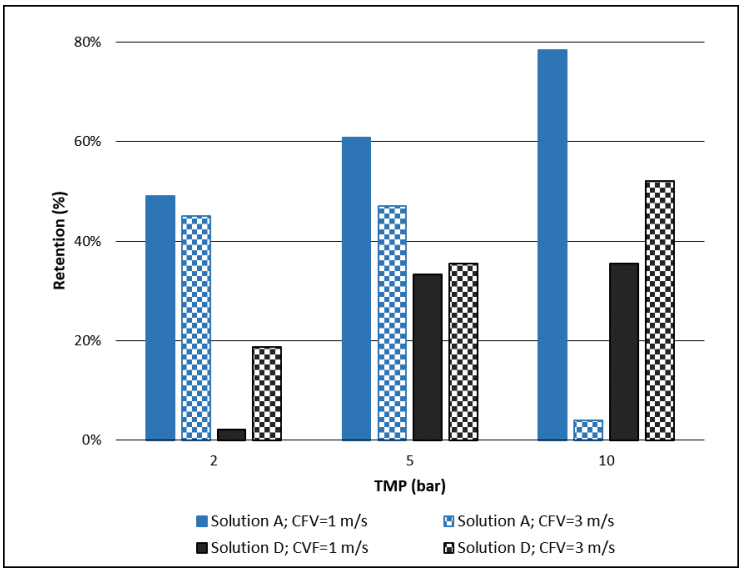


Figure 29: Comparison of the influence of TMP and CVF on retention of sucrose in Solution A and Solution D using Membrane LC1.

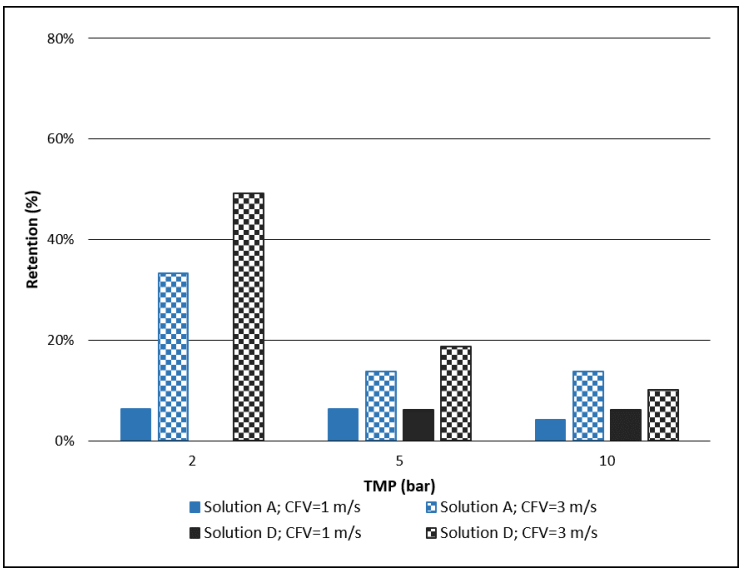


Figure 30: Comparison of the influence of TMP and CVF on retention of sucrose in Solution A and Solution D using Membrane LC2.

For Membrane LC1, Figure 29 shows that at a CFV of 1 m/s, the retention of sucrose during filtration of Solution A was greater than for Solution D and both increased with TMP. The difference between these retentions indicate that the presence of glucose and fructose in Solution D was influencing sucrose retention. Once again, the increase of the retention levels with TMP may be due to the concentration polarization phenomenon, as already explained. For a CFV of 3 m/s, the retention levels of each solution show opposite results: the retention of sucrose during filtration of Solution A decreased with increasing TMP while in

Solution D increased. The increase in sucrose retention with TMP, when filtering Solution D, suggests that the presence of glucose and fructose may had been increasing the phenomenon of concentration polarization.

For Membrane LC2, Figure 30 shows that for both CFVs tested there was a reduction of sucrose retention with increasing TMP, when filtering Solutions A and D. Sucrose retention in both solutions was quite similar, suggesting that Membrane LC2 may had not been so affected by concentration polarization phenomena when filtering a solution with various sugars as Solution D.

Overall, the results presented above allow to conclude that Membrane LC1 is the most suitable membrane, as it not only retains the sucrose in a single sugar solution, but as well as in a solution with different types of sugars. Furthermore, the retention results also support the findings obtained from the analysis of the permeate fluxes in Section 2.5.

4.4 Membrane Performance

The results provided in the membrane screening phase allowed to conclude that the Membrane LC1 is the one that provided the best fluxes and, more importantly, the greater retention of sucrose molecules. Hence, the permeation of Solution A was tested under 60°C and 80°C to assess the influence of temperature on permeate flux and retention levels given by Membrane LC1. Detailed data related to the membrane performance results can be found in Appendix E.

Permeate Fluxes

In Figure 31 is shown the permeate fluxes when performing the parametric studies at 60°C, 70°C and 80°C. The results obtained at 70°C were obtained in the screening phase and are now shown again.

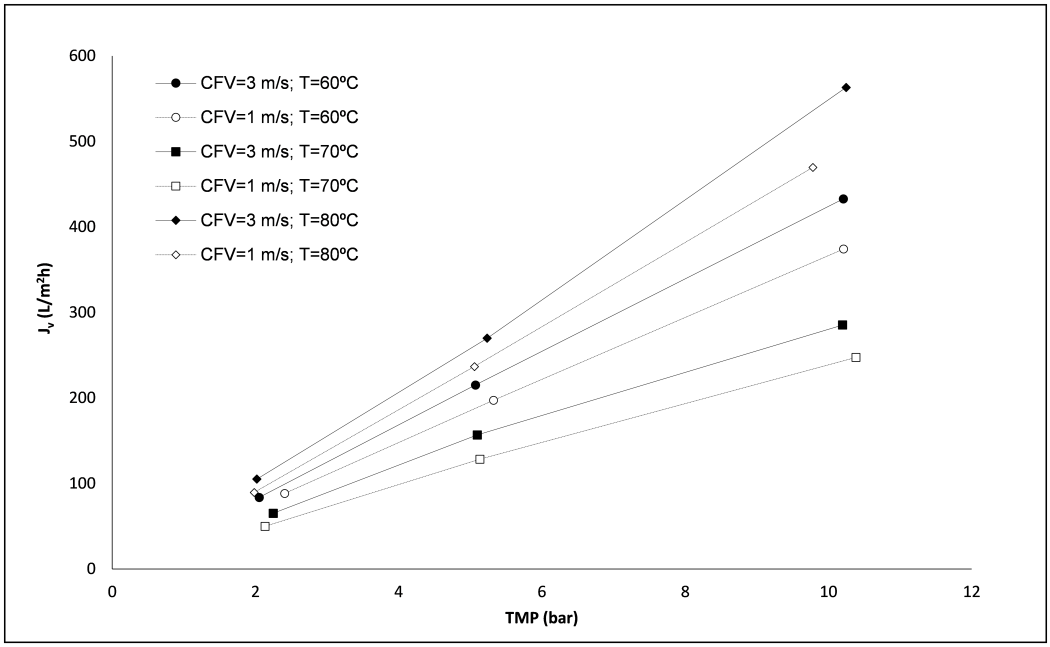


Figure 31: Influence of the temperature on the permeate fluxes of Solution A.

Figure 31 shows that, regardless of the temperature tested, the permeate fluxes increased with TMP and CFV. The highest permeate fluxes were obtained by performing the experiment at 80°C which is explained by the reduced viscosity at higher temperatures. As previously mentioned, sucrose is a disaccharide that when subjected to high temperatures will degrade into monosaccharides. These molecules have a lower MW than sucrose molecules and much lower than the MWCO of the membrane, therefore they will be more easily transported through the pores, thereby increasing the permeate flux. This hypothesis will be confirmed by the retention levels presented below.

The lowest permeate fluxes were obtained by performing the experiments at 70°C which it was not expected. Taking into account what has just been said about the thermal degradation of the sucrose molecules, it would be expected that the lower permeation fluxes would be obtained at 60°C, the lower temperature. Considering that the experiments at 60°C and 80°C were the last ones to be performed, it has to be considerer the possibility of some damage of the membrane, which may had caused these unexpected high permeate fluxes. Nevertheless, it is difficult to be certain of the cause for the high fluxes.

Retention Levels

Figure 32 shows the influence of temperature on the retention levels when filtering Solution A.

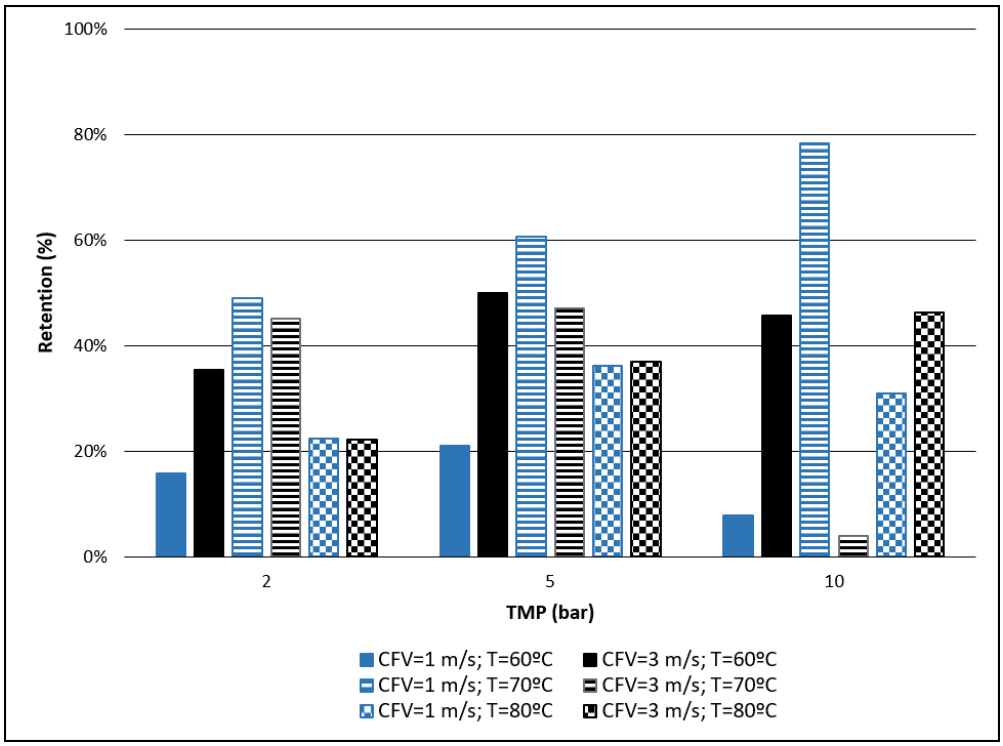


Figure 32: Influence of the temperature on the retention levels during filtration of Solution A.

Experiments carried out at 80°C showed the lowest retention values, which is in agreement with the hypothesis that sucrose molecules in Solution A started to degrade into smaller ones. The retention levels at 60°C were barely influenced by TMP and CFV and were lower than those at 70°C. The highest retention of sucrose molecules, around 80%, was obtained when performing the experiments at 70°C, a CFV of 1 m/s and a TMP of 10 bar.

4.5 Membrane Cleaning

The membrane cleaning is one of the most important steps when it comes to a membrane process, as it influences the membrane performance and, therefore, the physical and economic feasibility of the project. It is necessary to find the correct cleaning agent and cleaning procedure for each membrane.

Information concerning the cleaning procedure is given in Section 3.4.1. To assess on the effectiveness of the membrane regeneration, three different parameters were measured: PWF (J_{wi}), PWF of the fouled membrane (J_{w*}) and PWF of the cleaned membrane (J_w). Figure 33 shows the values related to the regeneration of Membrane LC1 during experiments with Solution B.

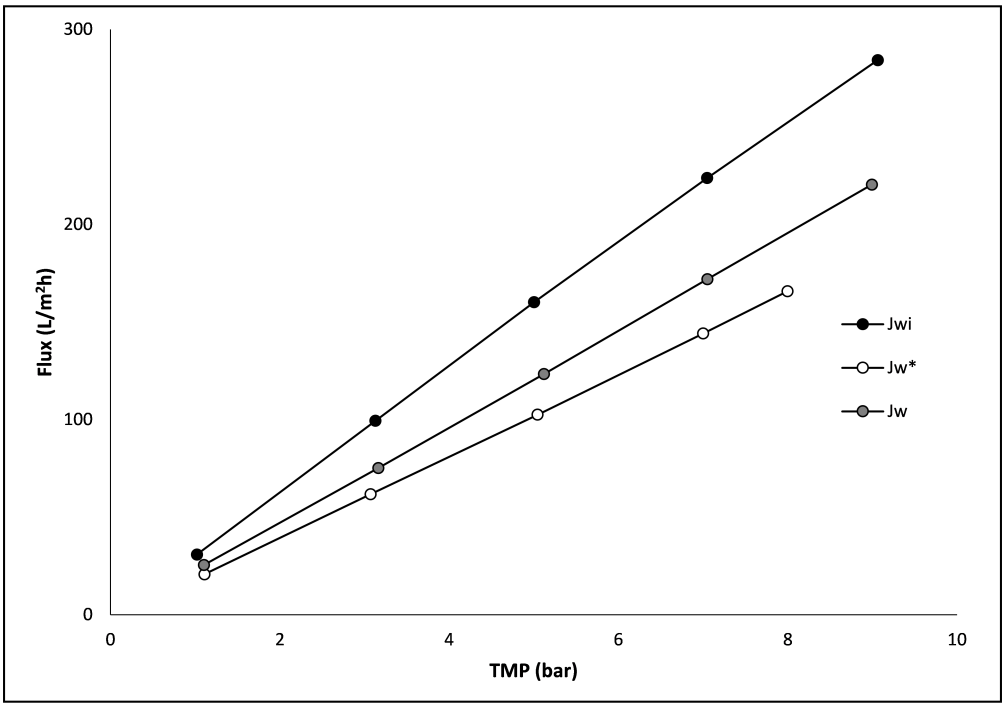


Figure 33: Pure water flux of the new membrane (J_{wi}), pure water flux of the fouled membrane (J_{w^*}) and pure water flux of the cleaned membrane (J_w) as function of TMP. T=30°C and CFV=3 m/s.

Figure 30 shows a decline of PWF after the experiments (J_{w*}), which was most likely to be caused by the fouling of the membrane. However, after performing the cleaning procedure, it was possible to recover part of the initial PWF, although not to its initial extent.

The measurement of the PWF at different stages of the experiments provided the necessary data to determine the hydraulic permeability before and after the membrane was cleaned, L_{pw*} and L_{pw}. These current parameters allows to asses on the degree of fouling of the membrane before and after the cleaning, $F_b(\%)$ and $F_a(\%)$, presented in Table 8.

$$\%F_b = \left(1 - \frac{L_{pw*}}{L_p}\right) \cdot 100 \tag{16}$$

$$\%F_a = \left(1 - \frac{L_{pw}}{L_p}\right) \cdot 100 \tag{17}$$

Table 8: Degree of fouling before and after the cleaning, $F_b(\%)$ and $F_a(\%)$.

	Membrane LC1		**Membrane LC2**	
	F_b	F_a	F_b	F_a
Solution A	63%	44%	77%	61%
Solution B	33%	22%	51%	48%
Solution C	26%	0%	66%	59%
Solution D	42%	0%	65%	5%

First, it is important to refer that all the hydraulic permeability values were corrected to a temperature of 25°C. The results shown in Table 8 indicate that both Membranes LC1 and LC2 were fouled after the filtration of each solution. The cleaning procedure decreased the degree of fouling in both membranes, but in different proportions and with different efficiency depending on the solution that was filtered.

The effect of the cleaning procedure was higher for Membrane LC1, since the difference between F_b and F_a was high. The lower values of F_a in Membrane LC1 indicate that the cleaning method and cleaning agent are suitable to be use in this membrane.

Regarding Membrane LC2, the F_b values were very high, indicating that the membrane was prone to fouling. After cleaning Membrane LC2, the degree of fouling did not decrease as must as it should, as the F_a values were in most cases higher than 50%. The low decrease of degree of fouling shows that the cleaning was not effective which may be related to the cleaning agent itself or the procedure. Thus, a new cleaning procedure and cleaning agent should be considered.

5 Conclusions

The current project consisted in the study of a nanofiltration membrane process to recover sucrose from sugar beet molasses. It was selected two tubular ceramic membranes with different MWCO, Membranes LC1 (200 Da) and LC2 (350 Da). Four solutions with different sugar composition were tested: Solution A (0.5%wt sucrose), Solution B (0.5%wt glucose), Solution C (0.5%wt fructose) and Solution D (0.5%wt of sugar of which 98% sucrose, 1% glucose and 1% fructose). Parametric studies were performed in order to assess on the most suitable membrane and operating conditions to achieve the desired separation. Furthermore, a detailed characterization of a sugar beet molasses sample provided by *Nordic Sugar* was executed.

The molasses sample has a sugar content of 470 g sucrose/g molasses, <1 g glucose/g molasses, <1 g fructose/g molasses and 10 g raffinose/g molasses.

The pure water flux of each membrane was measured allowing the determination of the hydraulic permeability. Membranes LC1 and LC2 have an hydraulic permeability of 28.2 and 20.5 L/hm^{2}bar.

From the parametric studies were obtained permeate fluxes and retention results. Regarding Membrane LC1, all solutions show an increase of their permeate fluxes with TMP and CFV. Solution A shows the lowest permeate fluxes possibility due to the high retention of sucrose. Solutions B and C show similar permeate fluxes and the highest ones. Solution D has intermediate permeate fluxes due to its composition. The retention of sucrose when filtering Solution A goes up to 80%, and the retention of glucose and fructose when filtering Solutions B and C is low, indicating that Membrane LC1 was permeating these molecules. Regarding the filtration of Solution D, the sucrose retention was not as high as for Solution A but still around 50%. About Membrane LC2, the permeate fluxes of Solution A are not influenced by CFV and are higher than Solution D fluxes, indicating that retention of sucrose is probably higher in Solution D. Solutions B and C show the highest permeate fluxes due to high permeation of their components, glucose and fructose. The filtration of each solution by Membrane LC2 provides low retention levels, not higher than 50%.

Comparing both membranes, Membrane LC1 provides higher permeate fluxes and higher retention of sucrose when filtering Solutions A and D than Membrane LC2. These specific results make Membrane LC1 most suitable to recover sucrose from sugar beet molasses.

After selecting Membrane LC1 as the most suitable, its performance was tested under temperatures of 60°C and 80°C, to compare with the results already obtained at 70°C. At 80°C permeate fluxes were the highest but retention levels were the lowest. At 60°C, both permeate fluxes and retention levels were not influenced by TMP and CFV. Permeate fluxes at 70°C were the lowest but it was obtained the best retention levels confirming the results of the screening phase. Furthermore, the highest retention of sucrose was around 80% when operated at 70°C, CFV of 1 m/s and TMP of 10 bar.

Different cleaning methods and cleaning agents were selected for each membrane. The cleaning of Membrane LC1 was more effective, having the degree of fouling decreased down to 0% in some experiments. Regarding Membrane LC2, a new cleaning method/agent should be considered since degree of fouling after cleaning exceed 50% in most cases.

5.1 Perspective of Future Work

The work presented in this report consisted only in the beginning of a much more complex project. These are some of the suggestions for future work to be done:

- Perform studies with molasses solution: The molasses have different composition and properties than the model sugar solutions tested in the project, therefore is expected that all the tests performed with the molasses will provide different results.
- Perform concentration studies: Due to technical problems with Membrane LC1 it was not possible to perform concentration studies. Nevertheless, the concentration studies with the molasses sample will provide important information regarding the membrane performance and parameters such as volume reduction;
- Evaluate membranes with different MWCO: The tested membranes had a high difference in MWCO and since the goal is to recover sucrose (342.3 Da), membranes with intermediate MWCO should also be considerer, e.g. 250 Da and 300 Da.
- Improve membrane cleaning: As shown in Section 4.5, the cleaning of Membrane LC1 was effective but it is important to consider that molasses are a very viscous product that will difficult the cleaning of the membrane. Thus, it is need to consider a new cleaning method and agent for the molasses filtration. Furthermore, the cleaning method/agent of Membrane LC2 should also be change.
- Evaluate a wider range of CFVs and TMPs: The use of ceramic membranes, which are very resistant, allow to operate at higher TMPs and CFVs. The performance of experiments with different parameters will provide a wider range of results that can or not be better than those already obtained.
- Study design configurations in series/parallel: The performance of experiments in series/parallel should be done since it can have an impact on the results, energy demand and capital costs;

- Perform an economical evaluation of the process: After the project is concluded it is important to make an assessment of the capital costs in order to decide if the project is economically viable or not .

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Appendix

A Module Information

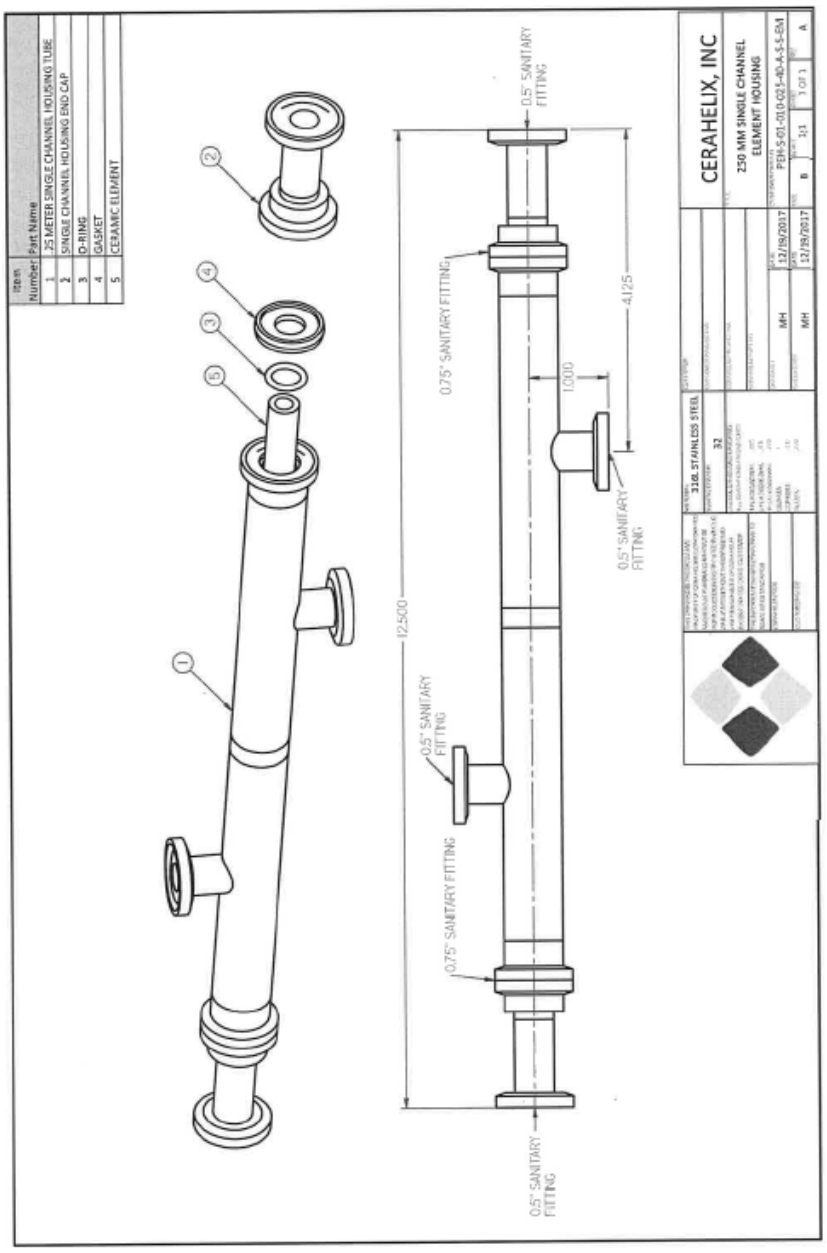

Figure 34: Module Specifications

B Analysis

Table 9: Data related to the determination of total solids and ash content of molasses samples.

Crucible	Crucible Weight (g)	Wet Weight (g)	Dry Weight (g)	Ash Weight (g)	Total Solids (%)	Ash (%)
M_A	52.7204	64.1456	61.1895	55.2473	13.2	22.1
M_B	52.7676	62.2679	58.8089	54.9508	9.7	22.9
M_C	53.3967	62.9761	60.4982	55.6084	11.3	23.1

C Pure Water Fluxes

Table 10: Results of PWF for Membranes LC1 and LC2. T=30°C.

Membrane LC1		Membrane LC2	
TMP (bar)	Flux $(\mathrm{L/m^2h})$	TMP (bar)	Flux $(\mathrm{L/m^2h})$
1.0	30.9	1.0	23.1
3.1	99.4	3.0	69.9
5.0	160.2	5.2	118.9
7.0	223.8	7.0	160.6
9.1	284.2	9.0	207.0

D Membrane Screening

D.1 Permeate Fluxes

Table 11: Results of the parametric studies for Membrane LC1. T=70°C.

	3 m/s		1 m/s	
	TMP (bar)	**Flux** $(\mathbf{L/m^2h})$	**TMP (bar)**	**Flux** $(\mathbf{L/m^2h})$
Solution A	2.2	65.3	2.1	49.9
	5.1	156.9	5.1	128.6
	10.2	285.4	10.4	247.5
Solution B	2.2	87.7	2.1	88.9
	5.1	212.5	5.2	215.3
	10.1	425.2	10.3	371.4
Solution C	2.1	92.7	2.2	95.8
	5.2	226.8	5.1	223.9
	10.2	436.5	10.5	449.7
Solution D	2.1	122.7	2.2	77.7
	5.2	270.1	5.2	190.1
	9.2	414.6	10.3	349.9

Table 12: Results of the parametric studies for Membrane LC2. T=30°C.

	3 m/s		1 m/s	
	TMP (bar)	**Flux** $(\mathbf{L/m^2h})$	**TMP (bar)**	**Flux** $(\mathbf{L/m^2h})$
Solution A	2.3	16.0	2.1	18.4
	5.2	70.3	5.4	82.2
	10.1	227.5	10.4	239.2
Solution B	2.1	55.0	2.1	25.6
	5.1	137.1	5.1	94.6
	10.1	303.4	10.3	260.5
Solution C	2.1	21.6	2.2	19.6
	5.1	62.1	5.0	68.7
	10.3	213.9	10.2	245.5
Solution D	2.1	25.4	2.2	15.2
	5.1	76.6	5.1	64.3
	10.2	225.4	10.2	196.2

D.2 Retention Levels

Table 13: Results of the retention levels of Membranes LC1 and LC2. T=70°C and CFV=1 m/s.

	Membrane LC1			**Membrane LC2**		
Solution/ TMP	**2**	**5**	**10**	**2**	**5**	**10**
A	49%	61%	78%	6%	6%	4%
B	1%	5%	25%	6%	7%	17%
C	6%	0%	0%	0%	10%	5%
D	2%	33%	35%	0%	6%	6%

Table 14: Results of the retention levels of Membranes LC1 and LC2. T=70°C and CFV=3 m/s.

	Membrane LC1			**Membrane LC2**		
Solution/ TMP	**2**	**5**	**10**	**2**	**5**	**10**
A	45%	47%	4%	33%	14%	14%
B	3%	18%	19%	3%	6%	25%
C	0%	0%	12%	0%	3%	43%
D	19%	35%	52%	49%	19%	10%

E Membrane Performance

E.1 Permeate Fluxes

Table 15: Results of the permeate fluxes of Membranes LC1. T=60°C, 70°C and 80°C.

	3 m/s		**1 m/s**	
Temperature	**TMP (bar)**	**Flux** $(\mathbf{L/m^2h})$	**TMP (bar)**	**Flux** $(\mathbf{L/m^2h})$
60	2.1	83.8	10.2	374.2
	5.1	215.3	5.3	197.4
	10.2	432.8	2.4	88.5
70	2.2	65.3	2.1	49.9
	5.1	156.9	5.1	128.6
	10.2	285.4	10.4	247.5
80	2.0	105.2	9.8	469.8
	5.2	269.9	5.1	236.9
	10.2	563.1	2.0	89.7

E.2 Retention Levels

Table 16: Results of the retention levels of Membranes LC1. T=60°C, 70°C and 80°C.

	CFV 1 m/s			CFV 3 m/s		
T°C/TMP (bar)	**2**	**5**	**10**	**2**	**5**	**10**
60	16%	21%	8%	35%	50%	46%
80	49%	61%	78%	45%	47%	4%
70	22%	36%	31%	22%	37%	46%

F Membrane Cleaning

Table 17: Results of the cleaning of Membrane LC1.

	Before Cleaning		After Cleaning	
	TMP (bar)	**Flux** $(\mathbf{L/m^2h})$	**TMP (bar)**	**Flux** $(\mathbf{L/m^2h})$
Solution A	1.1	12.2	1.1	17.1
	3.0	34.6	3.1	51.0
	5,1	58.3	5.1	85.0
	7.1	82.6	7.0	121.4
	9.0	105.0	9.0	156.0
Solution B	1.1	20.7	1.1	25.5
	3.1	61.8	3.2	75.2
	5.0	102.6	5.1	123.4
	7.0	144.1	7.0	172.0
	8.0	165.9	9.0	220.4
Solution C	1.0	22.7	1.1	44.3
	3.0	69.4	3.1	128.8
	5.1	117.8	5.0	207.5
	7.0	163.2	7.1	288.7
	9.1	211.6	9.1	366.5
Solution D	1.0	14.3	1.1	36.3
	3.1	53.8	3.1	101.1
	5.0	88.0	5.1	165.1
	7.1	125.3	7.1	231.0
	9.0	159.5	9.2	297.4

Table 18: Results of the cleaning of Membrane LC2.

	Before Cleaning		After Cleaning	
	TMP (bar)	**Flux** $(\mathbf{L/m^2h})$	**TMP (bar)**	**Flux** $(\mathbf{L/m^2h})$
Solution A	1.0	4.1	1.0	4.4
	3.0	9.3	3.1	16.4
	5.1	18.3	5.0	31.8
	7.1	30.0	7.1	49.7
	9.1	47.3	9.0	77.4
Solution B	1.0	9.0	1.0	8.5
	3.0	27.7	3.0	29.0
	5.0	47.8	5.1	58.1
	7.1	72.2	7.1	81.0
	9.0	100.3	9.3	105.5
Solution C	1.1	3.2	1.0	8.2
	3.0	14.0	3.2	23.5
	5.1	26.4	5.1	41.7
	7.2	43.4	7.0	58.1
	9.0	65.9	9.4	87.7
Solution D	1.1	2.4	1.0	9.5
	3.0	12.5	3.0	37.0
	5.1	25.5	5.0	80.8
	7.1	43.8	7.1	134.2
	9.0	65.6	9.1	181.1