Experimental Investigation of Nanofiltration Process for the Separation of Complex Sugar Mixtures Containing Mono- and Multivalent Salts

Muhammad Ali Samee*, Amal Ahmed Elgohary, Michael Harasek, Anton Friedl0

Institute of Chemical Engineering, Vienna University of Technology, Gertreidemarkt 9/166, A - 1060 Vienna, Austria
muhammad.ali.samee@tuwien.ac.at

The energy consumption of sugar producing industry is enormous mainly due to the thermal energy demand of multi-stage evaporation. However, alternative processes have been studied to reduce the high operating cost. Membrane technology is a well-established process for water treatment. Reverse osmosis (RO) and nanofiltration (NF) have also been examined for the pre-concentration of clarified thin sugar juice to reduce the role of evaporation in the sugar production process. RO/NF can be used to remove water from the aqueous solution at a temperature below its boiling point and without phase change. It has a positive effect on the quality of the clarified thin sugar juice because sugar juice is degraded at high temperatures. The clarified thin sugar juice contains 15 °Brix (15 w%) of sugar and about 0.25 - 0.40 w% of the ionic compounds. In the present work the effect of the presence of monovalent and multivalent salts on the separation performance of a nanofiltration membrane during sugar concentration has been studied experimentally. The sugar rejection was not affected much by the salt concentration but the rejection of monovalent or multivalent ions was found to be highly dependent on the sugar concentration.

1. Introduction

Sugar production is amongst the most energy extensive processes and therefore has a promising area of interest for researchers to look for energy efficient and environmentally friendly alternatives. Membrane technology is a novel process. It can be applied to aqueous solutions for the removal of water without changing the phase, with less energy consumption and thermal damage to the solution. Nanofiltration (NF) has been reported to be used for the concentration of thin sugar juice and removal of non-sugar components to minimize the load of non-sugars during the crystallization process (Gul et al., 2012). With increasing concentration of the sucrose solution the osmotic pressure and viscosity of the solution increases exponentially, therefore, thin sugar juice can only be concentrated economically from 15 w% up to 20 - 25 w% by membrane application due to this high osmotic pressure barrier (Gul et al., 2011). Thin sugar juice contains 0.25 - 0.40 w% of ionic compounds (Pinacci et al., 2001).

1.1 Nanofiltration (NF)
Nanofiltration is a type of pressure-driven membrane process with properties in between reverse osmosis (RO) and ultrafiltration (UF). In comparison with UF and RO, NF has always been a difficult process to define and to describe. Tight NF membranes are in some ways similar to RO membranes and open NF membranes could probably be classified as UF membranes. NF offers several advantages such as low operating pressure, high flux, high retention of multivalent anions and organic solutes with molecular weight above 300 Dalton, relatively low investment and low operation and maintenance costs (Vellenga et al., 1998). NF membranes are characterized by pore diameters and operating pressures. Because they significantly reject many ions, NF membranes are often wrongly categorized as "loose RO" membranes. The most important difference between RO and NF is the ability of NF to highly reject multivalent ions, while significantly allowing the passage of

monovalent ions. The separation capability of NF membrane is directly related to the membrane material properties. Experimentally the permeate flux (J_p) in kg/m²h can be calculated by Eq(1).

$$J_p = \frac{m}{t.A}$$ (1)

Where m is the mass of the permeate (kg), t is the time (h) and A is the membrane area (m²). A commonly used parameter to describe the membrane separation performance is the rejection coefficient (R_i) given by Eq(2).

$$R_i = (1 - \frac{c_{i,permeate}}{c_{i,feed}}) * 100\ \%$$ (2)

Where c is the concentration.

Concentration polarization is an important phenomenon in NF membranes which refers to the reversible accumulation of rejected solute particles close to the membrane surface. In membrane processes all the components in the feed are transported to the membrane surface by convection and this rate increases with the increasing permeation. The selectivity of the membrane retains the less permeable components. At the steady state, these less permeable components have to be transported back into the bulk of the feed stream. As the flow next to the membrane surface is laminar, this transport can only be diffusive. The transport has to be based on the established concentration gradient, i.e., an enrichment of the less permeable components at membrane surface. It is a natural consequence of membrane selectivity. If the driving force is removed, the permeation ceases and the concentration polarization phenomenon disappears.

NF membranes have been reported to inherit three types of pore blockage phenomena namely complete pore blocking restricting the transport of both water and solute, intermediate pore blocking and standard pore blocking allowing water transport and reducing the effective pore size of the membrane (Bellona et al., 2010).

2. Experimental setup

The experiments were conducted on a lab-scale cross-flow membrane unit OS-MC-01 from Osmota with an effective membrane area of 0.008 m² presented by Figure 1. In this work, a negatively charged NF membrane MPF-34 from Koch Membrane was used. It has a maximum operating temperature limit of 70 °C, a pressure range of 5 - 35 bar, and a pH range of 0 - 14. The deionized water permeability was measured before and after each experiment. Cleaning of the membrane was performed if de-ionized water permeability dropped by 10 % of the original value and cleaning procedure was adopted as per recommendations of the membrane manufacturer.
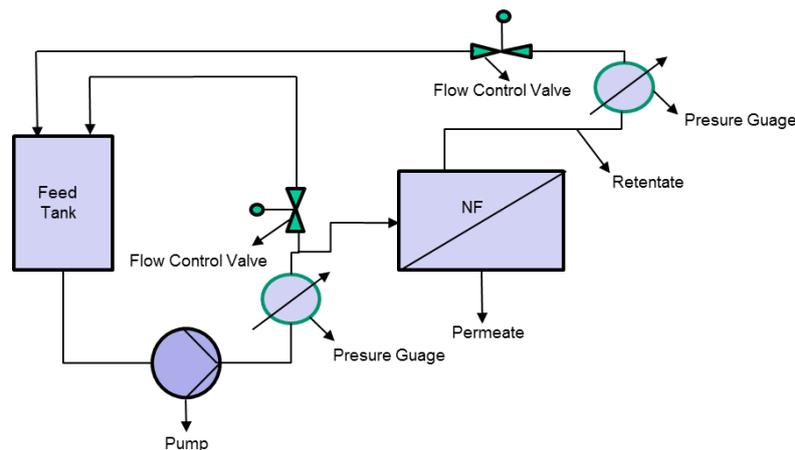
Figure 1: Influence of the sugar concentration on the permeate flux

Different possible combinations of monovalent and divalent cations and anions were formulated both as a single and mixture of salts mixed with sugar as shown in Table 1.

Table 1: Combinations of monovalent and multivalent cations and anions with sugar

Single salt with sugar	Mixture of salts with sugar
NaCl + sugar	NaCl + MgCl$_2$.6H$_2$O + sugar
MgCl$_2$.6H$_2$O + sugar	NaCl + Na$_2$SO$_4$ + sugar
Na$_2$SO$_4$ + sugar	NaCl + MgSO$_4$ + sugar
MgSO$_4$ + sugar	MgCl$_2$.6H$_2$O + Na$_2$SO$_4$ + sugar
	MgCl$_2$.6H$_2$O + MgSO$_4$ + sugar
	Na$_2$SO$_4$ + MgSO$_4$ + sugar

Pure refined sugar and high quality salts were used in the experiments. The deionized water was used to prepare salt and sugar solution. All the experiments were performed at the same process conditions of 32 bar, 60 °C, feed flowrate of 2.5 L/min, starting with a feed sugar concentration of 15 °Brix and 0.25 w% of each electrolyte mixed artificially with sugar. The temperature was kept constant by using a thermostat. The experiments were performed in re-circulation mode so that the feed concentration kept on increasing during the course of experiment. Samples of permeate and retentate were collected and the permeate weight was measured gravimetrically with an electrical balance in specified intervals of time to calculate the flux. Sugar concentration in permeate and retentate samples was measured by a digital refractometer DR301-95 from Krüss, while the concentrations of the dissolved anions and cations were analyzed on a Dionex ICS 5000$^+$ ion chromatography equipment.

3. Results and discussion

3.1 Permeate flux

The solvent flux is found to be dependent on viscosity, molecular size and surface tension between solvent and the membrane (Geens et al., 2006). The flux of the model sugar solution decreases with the sugar concentration from 65 kg/m^{2}h at 13 °Brix to less than 10 kg/m^{2}h at 24 °Brix. This is due to the increase in osmotic pressure and viscosity with the increasing sugar concentration and as a result the net driving force is decreased resulting in a lower permeate flux. The addition of a single monovalent/divalent salt or a complex mixture of both, in the sugar solution, contributes to increase the osmotic pressure resulting in less permeate flux than the flux value of model sugar solution. This addition does not affect the flux considerably but it gives the same decreasing trend as of model sugar solution identified in Figure 2.
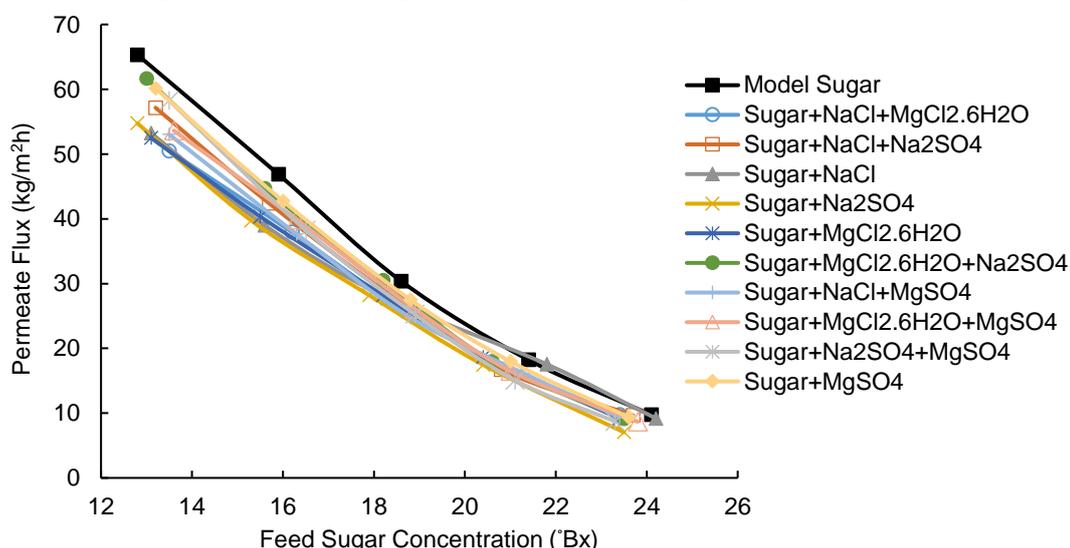
Figure 2: Influence of the sugar concentration on the permeate flux

3.2 Sugar rejection

The rejection of organic molecule by NF membrane is mainly due to steric (sieving) effect. The sugar rejection of the model sugar solution is very high and shows a very small decreasing trend with increasing feed sugar concentration and is of the order of 98 - 97 % as described in Figure 3. This very high sugar rejection can be expected to have hidden effects on transport phenomena (Vellenga et al., 1998). The sugar concentration has

no significant influence on the sugar rejection. Similarly, the addition of a single monovalent/divalent salt or a complex mixture of both in the sugar solution does not show a pronounced decrease in the sugar rejection and is in the range of 98 - 94 %.
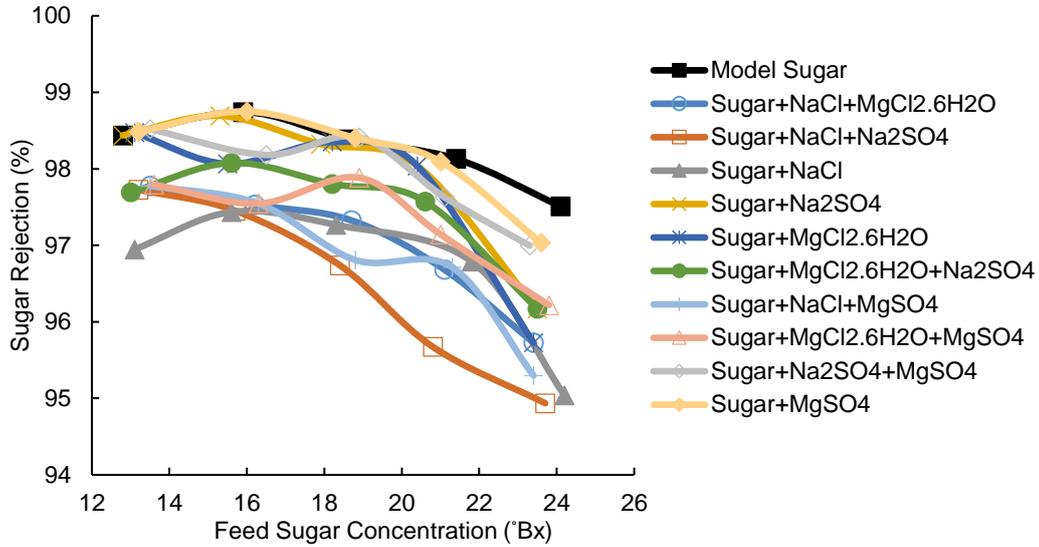
Figure 3: Effect of the sugar concentration on the sugar rejection

3.3 Ionic rejection

The ionic rejection of a NF membrane can be due to electrical effects. The rejection of salt by NF membrane is dependent of ionic concentration and charge density of the membrane (Vellenga et al., 1998). The rejection of monovalent cations e.g Na^+ has been investigated as a function of feed sugar concentration as represented in Figure 4. The rejection of Na^+ decreases with increasing sugar concentration. It demonstrates a varying degree of rejection from 94 % to - 21 % in a mixture of sugar, monovalent and/or multivalent cations and anions. This decrease in rejection could be due to the viscosity effect. The viscosity of the solution increases with increasing feed concentration. The higher rejection of the sugar causes the higher viscosity in the concentration polarization layer, as a result the back diffusion of the ions in the concentration polarization layer is restricted. This exhibits higher salt concentration in the concentration polarization layer and a decreased rejection. Monovalent ions can pass through the membrane to a greater extent.
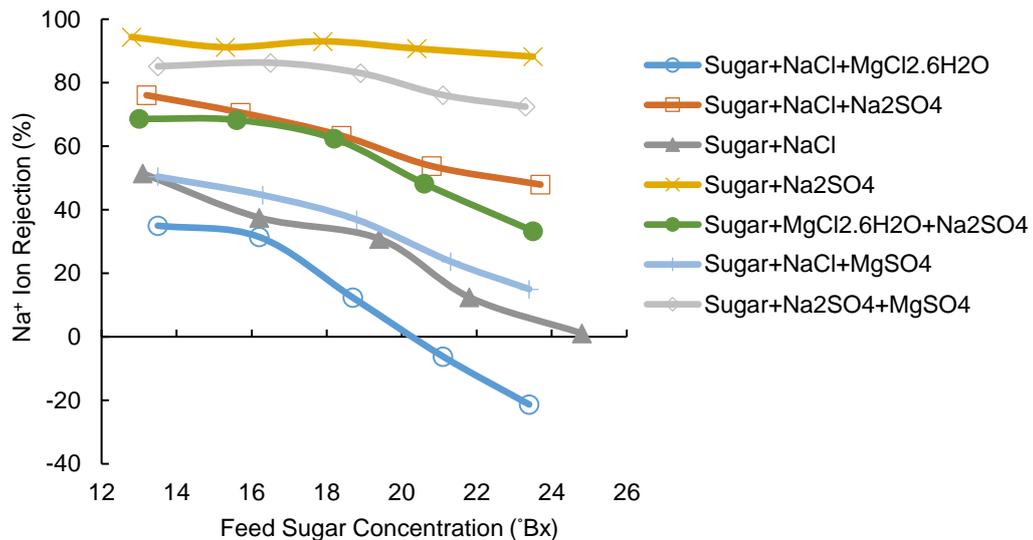
Figure 4: Rejection of Na^+ ion as a function of feed sugar concentration

Figure 5 explains the rejection of divalent cations e.g. Mg^{2+} as a function of sugar concentration. Mg^{2+} shows a higher rejection (> 88 %) in sugar, monovalent and/or divalent ionic mixtures.
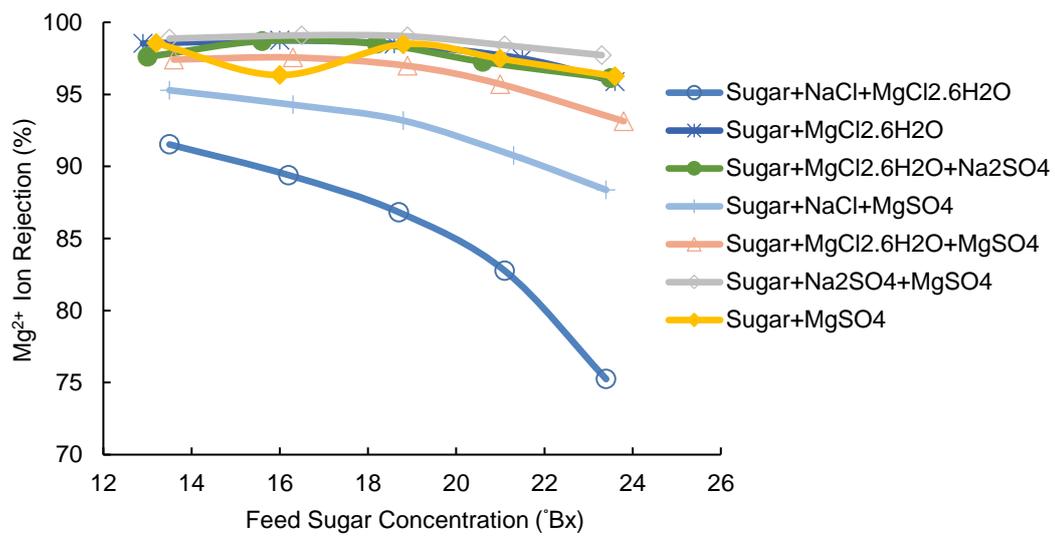
Figure 5: Rejection of Mg^{2+} ion as a function of feed sugar concentration

The rejection of monovalent anions e.g. Cl$^-$ has been investigated as a function of sugar concentration as depicted in Figure 6. The rejection of Cl$^-$ decreases with the increasing sugar concentration. It gives a varying degree of rejection from 98 % to -46 % in a mixture of sugar, monovalent and/or multivalent cations and anions. The NF membrane has an effective negative charge. As the concentration polarization layer builds up, the counter-ions gets preferably closer to the membrane surface charges and hide the surface charges partly with their increasing concentration. Now it is convenient for the co-ions to pass through the membrane because these ions face less electrical repulsive forces offered by membrane surface charge so the salt rejection decreases.
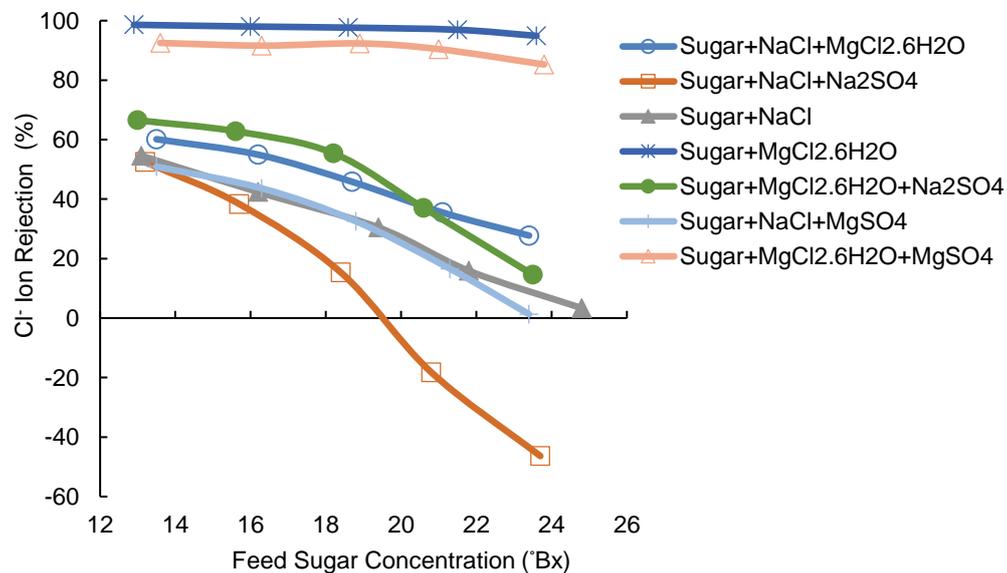
Figure 6: Rejection of Cl$^-$ ion as a function of feed sugar concentration

Figure 7 elaborates the rejection of divalent anions e.g. SO$_4$$^{2-}$ as a function of sugar concentration. SO$_4$$^{2-}$ presents a higher rejection (> 88 %) in the sugar, monovalent and/or divalent ionic mixtures.
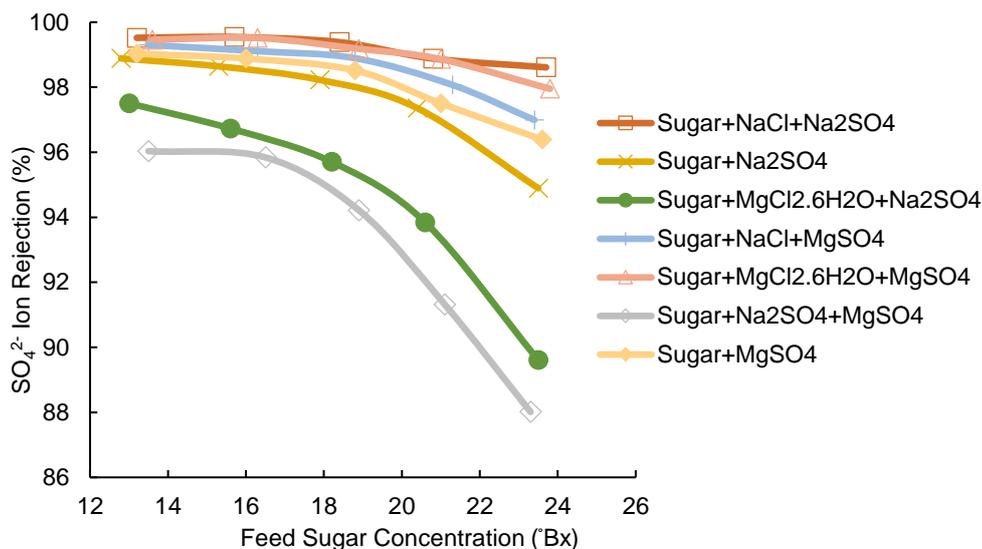
Figure 7: Rejection of SO$_4^{2-}$ ion as a function of feed sugar concentration

4. Conclusions

The permeate flux for aqueous solution of sugar and monovalent/divalent salt (single or mixture) decreases with the sugar concentration. In addition, it is dependent on osmotic pressure of the solution and pure water permeability of the membrane. Sugar rejection in all cases is always higher than 95 % and is not effected much by the sugar concentration and the salt concentration in the range studied. Na$^+$ gives negative rejection in the presence of sugar, monovalent anion and divalent cation and shows almost zero rejection in the presence of sugar and only one monovalent anion. Similarly, Cl$^-$ exhibits a negative rejection in the presence of sugar, monovalent cation and divalent anion and shows almost zero rejection in the presence of sugar and only one monovalent cation. It can be generalized that by adding sugar to different ionic mixtures with one ion with a maximum valence of 2 will govern the negative rejection of the corresponding monovalent ion as observed in case of Na$^+$ and Cl$^-$. Mg^{2+} and SO$_4^{2-}$ show a rejection greater than 90 % in most of the solutions containing sugar, monovalent and multivalent ions.

References

Bellona C., Marts M., Drewes J.E., 2010, The Effect of Organic Membrane Fouling on the Properties and Rejection Characteristics of Nanofiltration Membranes, Separation and Purification Technology, 74, 44-54.

Geens J., Van der Bruggen B., Vandecasteele C., 2006, Transport Model for Solvent Permeation Through Nanofiltration Membrane, Separation and Purificaton Technology, 48, 255-263.

Gul S., Harasek M., 2011, Energy Savings in Sugar Manufacturing with the Implementation of a new Membrane Process, Chemical Engineering Transactions, 25, 1085-1090.

Gul S., Harasek M., 2012, Energy saving in Sugar Manufacturing Through the integration of Environmental Friendly New Membrane Process for Thin Juice Pre-concentration, Applied Thermal Engineering, 43, 128-133.

Pinacci P., Radaelli M., Benedetto M.C., 2001, Demineralization of Thin Juice by Electrodialysis in the Beet Sugar Manufacturing Industry, Process Engineering with Membranes, Granada, Spain, June 3-6, 2001.

Vellenga E., Trägärdh G., 1998, Nanofiltration of Combined Salt and Sugar Solutions: Coupling between Retentions, Desalination, 120, 211-220.