Application of Membrane Distillation Crystallization towards the recovery of sugar from sugarcane extract.

Pheletso Marumoloe, Lebea Nthunya, Heidi Richards.

Environmental Analytical chemistry Group, school of Chemistry, University of the Witwatersrand, PO Wits 2050, Johannesburg, South Africa.

Heidi.richards@wits.ac.za , Pheletso.marumoloe8@gmail.com, Lebea.nthunya@wits.ac.za.

KEYWORDS:*Crystal size distribution, sugar production, membrane distillation crystallization, sugarcane, crystallization.*

ABSTRACT: A cutting-edge hybrid technique addressing the shortcomings and constraints of traditional pressure-driven membrane procedures that handle highly concentrated solutions is membrane distillation crystallization (MDC). In the study, sugar water was treated with the MDC technique to recover high-quality water and sugar crystals with uniform sizes and good crystal growth. The effect of temperature on the permeate water flux, growth and morphology, and particle size distribution was investigated by varying the feed temperatures. At 80^0C feed temperature, high quality water was determined to have a flux of 0.9 Kg m^{-2} h^{-1} and a recovery rate of 95%. A higher growth rate resulted as well at the highest feed temperature, 80^0C, but also suffered from agglomeration, seen from the particle size distribution plots and the optical microscope images. The study grows the understanding and development of the MDC technique towards the recovery of high-quality water and sugar crystals.

1. INTRODUCTION

Sugarcane is the main source of sugar, and therefore a key requirement in various industrial ingredients including food sweetening. In 2016, a total of 26,774,304 hectors was harvested, accounting for 1.93% of the world's harvested area, ranking it as the 12th most important crop globally.[1] In the same year, sugarcane production was 1,890,661,751 tons, making it the world's most important crop in terms of volume and accounting for 21.1% of total global crop production.[1] Sugar production is a large industry with a significant economic impact. It is an important ingredient in a wide range of food and beverage products, including confectionery, baked goods, beverages, and processed foods.[2] Sugar, in addition to being used in food, may be transformed into biofuels such as ethanol.[3]

Although sugar production from the cane is a key requirement for various processes, its production from the sugar cane extract requires cost effective processes capable of forming uniform crystal size distribution, crystal formation and growth. Membrane distillation crystallization (MDC) received a remarkable attention in resource recovery from various solutions. Its exploration in sugar cane crystallization offers a sustainable and economically viable option towards sugar production. The MDC is a hybrid technique of membrane distillation (MD) and conventional crystallization where high quality water is produced as a permeate from the MD process, while the case sugar is supersaturated and recovered as solids in the crystallizer.

Compared to other membrane processes such as reverse osmosis, nanofiltration (NF), the MDC operates at low pressures, low temperatures and presents the potential retention of nonvolatile solutes, thus achieving excellent purity of permeate water.[4] The MDC operates based on vapor-liquid equilibrium, with the membrane serving as a contactor between the two interfaces rather than as a separation unit. The process is driven by the vapour pressure

gradient induced by the temperature across the membrane interface. The operating feed temperatures range from 30 ºC to 80 ºC while the permeate temperature is maintained below 25 ºC thus offering an option of utilizing waste heat or renewable energy sources.[5] The MDC technology offers a wide range of applications, including desalination utilizing low grade heat, concentration of aqueous solutions and fruit juices, acid recovery, elimination of organic compounds in drinking water production, and radioactive waste treatment.[6,7]

Unlike conventional crystallizers, MDC achieves well-controlled nucleation and crystal development via uniform evaporation rate across the membrane holes. As a result, MDC produces substantially more desirable crystals in terms of purity and size distribution over conventional industrial crystallizers.[8] Traditional crystallization processes, such as batch vacuum pans or cooling crystallizers, are frequently used in today's sugar production technologies. These procedures do not yield uniform crystal sizes due to variations in cooling rates, agitation, and seeding processes influencing crystal distribution. Current technology allows for the regulation of crystal size via seeding and agglomeration operations.[9] Because of temperature polarization (Tp) and concentration polarization (Cp), the membrane surface temperature (Tw) is lower, and the concentration (Cw) is higher near the MD membrane surface compared to the bulk solution. These polarization processes are crucial in MDC since solubility varies with temperature. As a result, for aqueous salt solutions with a positive solubility-temperature coefficient (i.e., lower solubility at lower temperatures), such as sucrose, the combined polarization effects stimulate crystal formation on the membrane due to the reduced solubility near the membrane wall.[10] In the current study, sugar was produced for the first time from a simulated sugar cane in direct contact hollow fibre MDC. The effects of process temperature were evaluated to understand their impact on sugar crystal formation and size distribution.

2. EXPERIMENTAL PROCEDURE

2.1. Materials.

The Selati brand of sugar, which was used to make the synthetic feed solution, was purchased at a nearby Pick 'n Pay (South Africa) supermarket. The lab provided (synthesized at the lab) the distilled water that was needed to dissolve the sugar. A pre-synthesized hollow fiber polypropylene membrane module with 19 fibers was employed. These fibers had a length of 42 cm, an average pore size of 0,2 µm, and a surface area of 0,02 m^2. The membrane module has a 73% porosity and a 0.45 mm membrane thickness. The diameter of the inner and outer fibers are 1,8 and 2,7 mm respectively.

2.2. Methods.

The synthetic feed was prepared to closely mimic the properties of a sugarcane extract. Table 1 below lists the concentrations of the synthetic feed for the MD process. 250g of synthetic sugar were dissolved in 500mL of distilled water to prepare the feed solution.

Table 1: synthetic feed concentrations used in the study at different operational conditions.

Feed solution	Concentration of the feed solution. (mol/L)	Operational Temperature (°C)
Sugar	1,46	55

Sugar	1,46	65
Sugar	1,46	80

Direct contact membrane distillation (DCMD), in which both feed and permeate streams are in contact with the membrane, was used in this study. A hollow fibre membrane with a surface area of 0,02 m^2 was used for the isolated MD experiments. Bulk temperatures were measured by thermocouples. Flux was measured as weight gain in the cold permeate reservoir and recorded every five minutes. Feed solution was heated by a heating bath while the temperature of the permeate reservoir was kept constant by using a chiller. Feed and permeate were circulated counter-currently using a peristaltic pump (MasterFlex L/S). In these studies, MD feed temperatures used were 55, 65 and 80 ◦C and cold permeate temperatures was kept constant at 18 ◦C. The MD experiments were performed in a closed-circuit mode without the crystallizer to examine performance at extreme sugar concentrations. We have used three aqueous solutions of sugar crystals dissolved in water. The concentrations of the feed solutions were 1,46 M for the three aqueous feed solutions, and the initial feed volume was 500 ml for each run. Because feed and permeate outlet temperatures fluctuate with inlet temperatures, the outlet temperatures were observed. For example, at an operating temperature of 80 degrees for the feed and 18 degrees for the permeate, the feed's inlet and outlet temperatures were 53 and 49 degrees respectively, while for the permeate, the inlet and outlet were 18 and 20 degrees respectively. These temperatures were used to calculate the average temperature difference across the membrane interface using equations 1, 2, and 3.

$$\Delta T_{in} = T_{feed,in} - T_{permeate,out} \quad (1)$$

$$\Delta T_{out} = T_{feed,out} - T_{permeate,in} \quad (2)$$

$$\Delta T_{In} = \frac{\Delta T_{in} - \Delta T_{out}}{In\frac{\Delta T_{in}}{\Delta T_{out}}} \quad (3)$$

The water flux was determined by measuring the permeate's weight increase and using equation 4 to calculate the flux

$$J = \frac{dm}{Adt} \quad (4)$$

Where $J, dm, A, dt,$ represent water flux, mass difference at time (t), change in time.

A schematic of the MDC process at lab scale is given in the figure below.

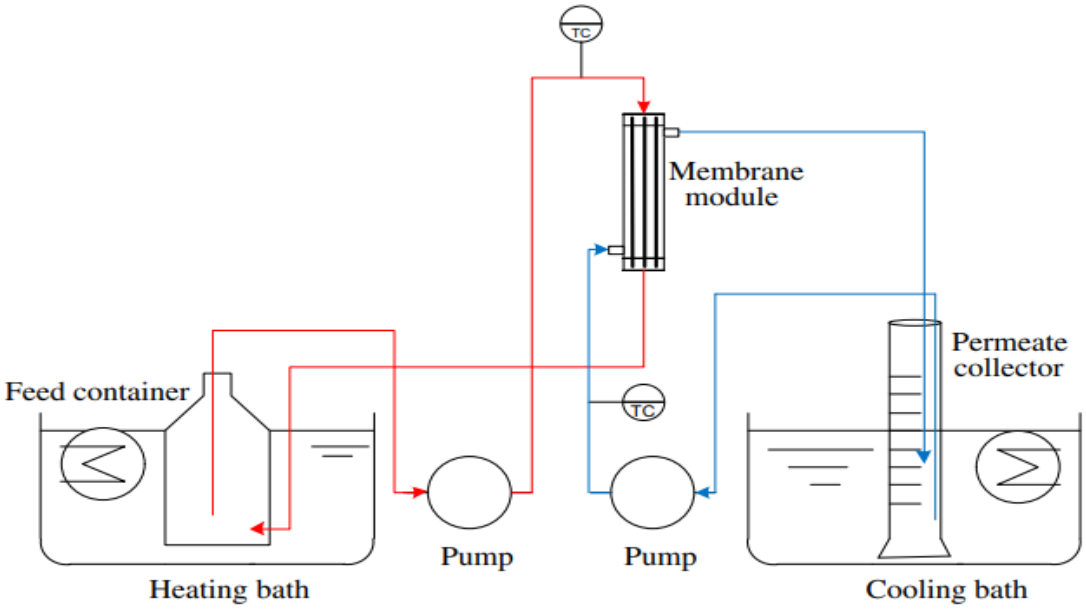


Figure 1: A schematic of the MDC system used for high quality water and mineral salts recovery.[11]

2.3. Crystal characterization.

Using an optical microscope, the growth and nucleation of crystals were observed. Using the resulting microscopic pictures, the particles were measured using ImageJ software. In order to guarantee an accurate representation of the particle size distribution, at least 100 crystals were examined. By measuring the particle length and applying equation 5 to derive the growth rate, the sugar crystal growth rate was calculated. Equation 6 gives the linearized form of equation 5, which was used to calculate Geff from the slope.

$$G^{eff} = \frac{1}{2}\frac{dL}{dt} \quad (5)$$

$$dL = 2G^{eff}dt \quad (6)$$

Where dL, dt, and G^{eff} were change in crystal length, growth time and effective growth rate. Constant factor $(\frac{1}{2})$ accounts for particle growth from crystal centre to two opposite directions.

3. RESULTS AND DISCUSSION

3.1. The effect of feed temperature on the permeate water flux.

The performance of the MDC process at various operating temperatures was evaluated using the acquired water flux data(Figure 2). Figures 2a and 2b show the plots of the pure water flux and the sugar water flux. The feed temperature of 80ºC produced the highest water flux, whereas the pure water flux at all three temperatures stayed relatively stable

shown by their comparatively constant plots. Plot stability for the sugar water flux was generally good, although for all temperatures, it started to decline after 10 h. The greatest flux between 0.8 and 0.9 Kg m^{-2} h^{-1} was obtained at a feed temperature of 80ºC, while the lowest flux between 0.5 and 0.6 Kg m^{-2} h^{-1} was obtained at a feed temperature of 55ºC. this is expected as the flux is affected by an increased temperature polarization.[12] Hence a higher feed temperature achieves a higher temperature polarization and a higher water flux. The drop in the stability of the water fluxes for the sugar water (Figure 2b) may be due to the sugar water reaching supersaturation, forming a syrup-like solution that fouls the membrane and destabilizes the flux.

Plots of the temperature gradient with time are displayed in Figure 2c. Notably, the maximum feed temperature of 80ºC is responsible for the significant deltaT. deltaT, which represents the driving force behind the MD process, varied somewhat throughout the course of the three temperatures but stayed largely stable. Plots show that the difference between feed temperature and the bulk feed temperature caused temperature polarization. The differential in vapour pressure that arises from the temperature polarization is what drives the separation of water.[13]

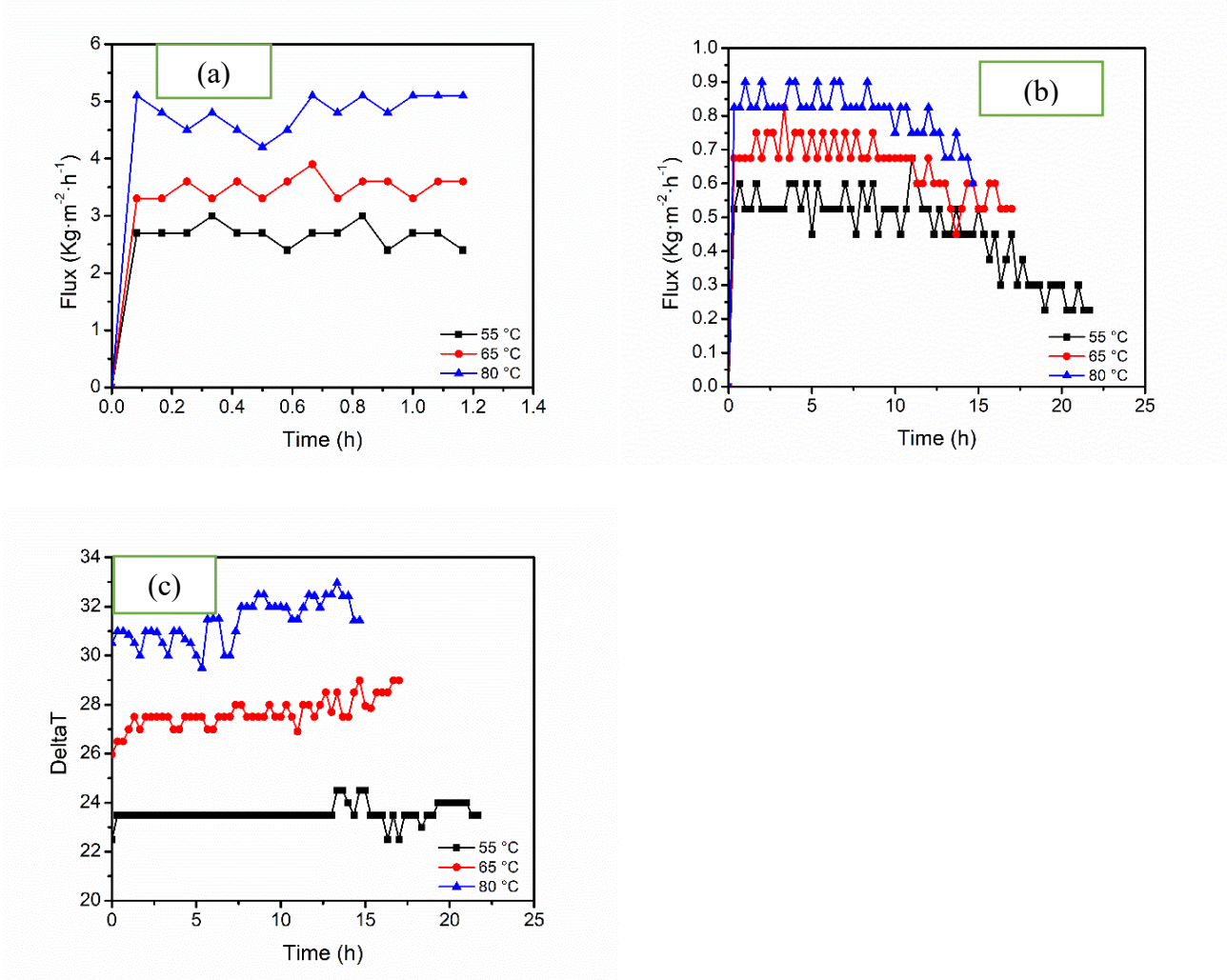


Figure 2: Test for the performance of MD process: (a) Pure water flux, (b) Sugar water flux and (c) Temperature gradient.

3.2. Change in water flux as a function of recovery factor

Figure 3 shows the water flux and deltaT reported as a function of recovery factor at different operational temperatures. There was only a slight decrease in DeltaT and flux due to temperature polarization. Low feed temperatures also showed notable flux and deltaT variations. For instance, at 55ºC feed temperature the flux varies between 0.25 to 0.6 Kg m^{-2} h^{-1}. Poor heat distributions between the bulk feed and the feed at the membrane interface could have been the factor for this seen trend for the low temperature feed (55ºC). The deltaT of the lower input feed temperature showed significant variations. The permeate flux dropped somewhat, while deltaT was basically constant as a function of recovery factor.

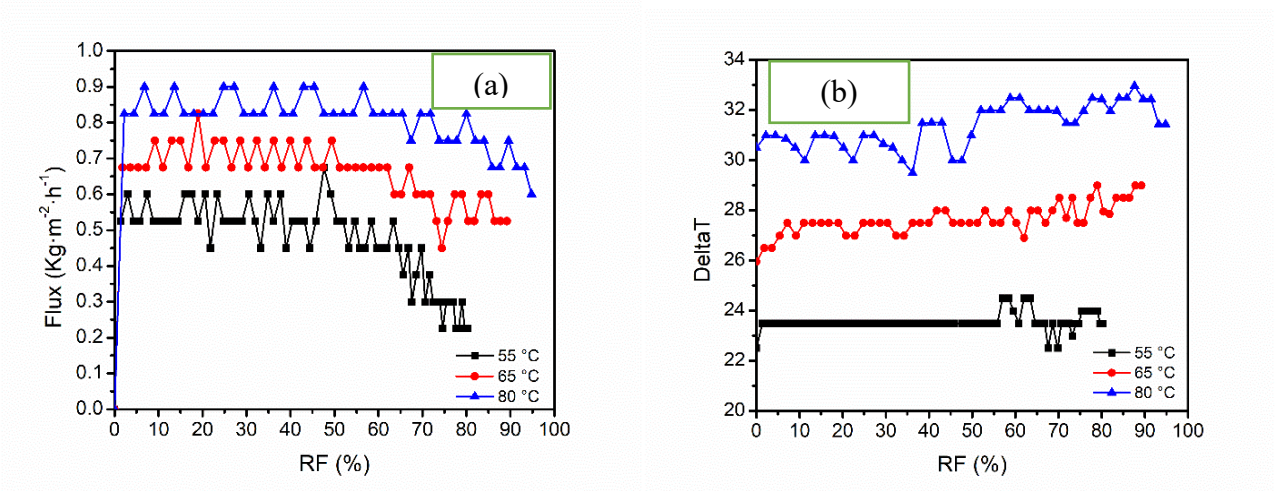


Figure 3: Water flux (a) and change in temperature across the membrane for three feed temperatures (b) as a function of recovery factor.

3.3. Growth and morphology of crystal structures.

An optical microscope with a magnification of 50x was used in the study to monitor crystal formation and growth. The images show that the crystals do not follow the anticipated hexagonal prism shape and instead appear to aggregate, which makes it difficult to determine the morphology with high confidence. The images in figure 4 show that this agglomeration process appears to occur frequently at high temperatures. The argument that operational temperature affects crystal development and formation has been confirmed by literature.[14] The images demonstrate that there is only an initial and agglomeration stage, which is also apparent for the agglomeration process, rather than the propagation stage.

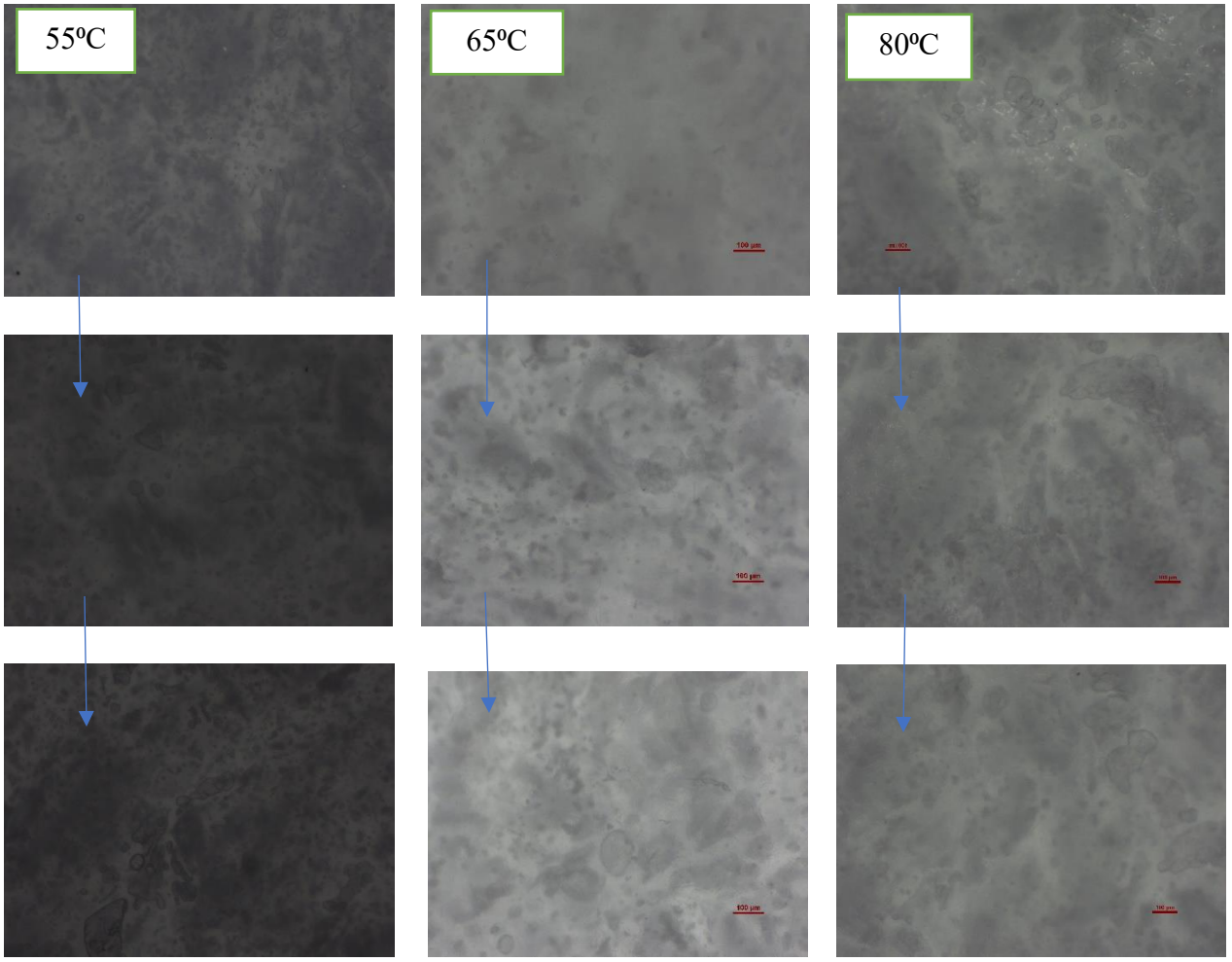
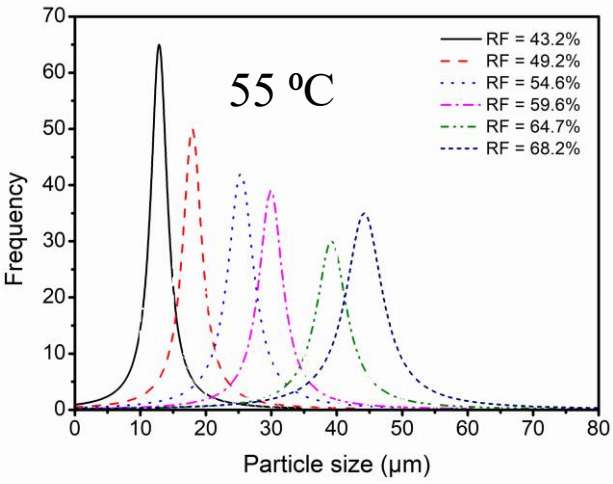
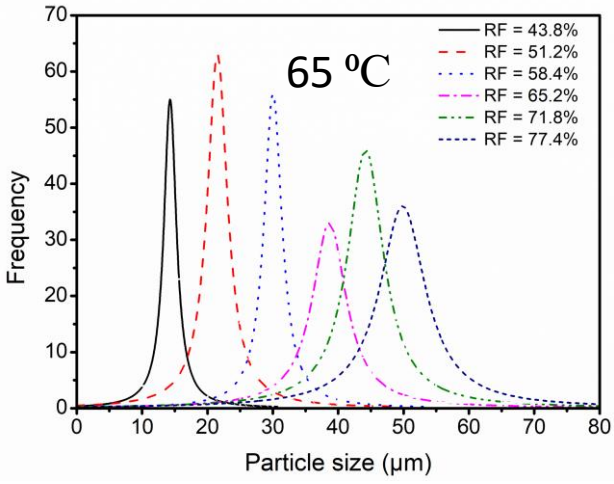


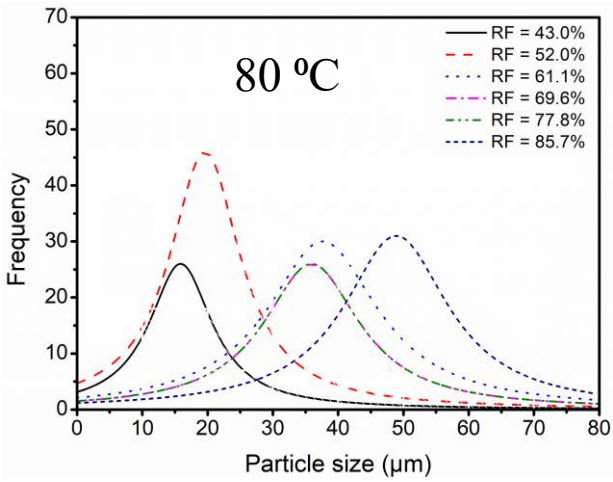
Figure 4: Optical microscope images of sugar water at 80ºC, 65ºC and 55ºC.

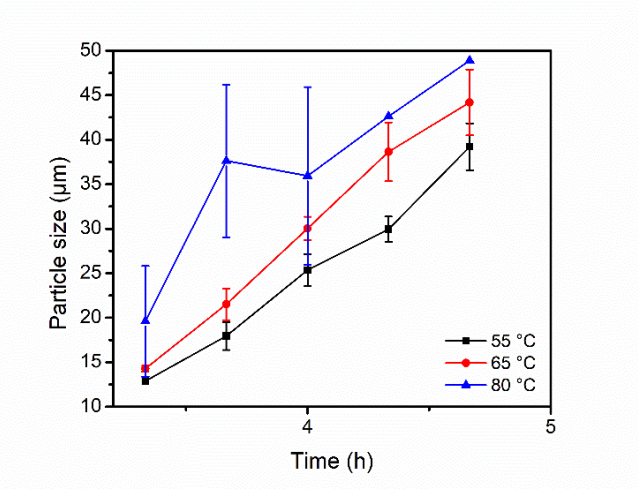
3.4. Effect of temperature on particle size distribution and growth rate

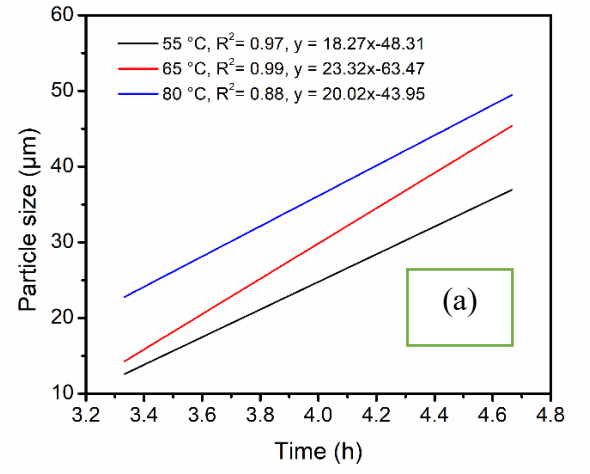
An optical microscope was used to evaluate the crystal size distribution, and the Lorentz non-linear model was used to determine the particle size distribution. Figure 5 below illustrates this information. There are narrow peak distributions as well as broad peak distributions, as can be seen in figures 5a, b, and c. In contrast to the broad peaks, where sugar crystals form dissimilar crystal structures with less uniformity, the narrow peak distributions illustrate sugar crystals that formed similar and uniform crystal structures. The broadening effect is more pronounced for the highest feed temperature, 80ºC, which provides additional support for the agglomeration process that had taken place. This may be because higher feed temperatures have faster growth rates. The 80ºC feed temperature in figure 5d has a higher growth rate than the 65ºC and 55ºC feed temperatures. This is because higher feed temperatures result in higher fluxes, which supersaturate the feed solution at a faster rate, leading to a higher crystal growth rate. The literature supports this by stating that the MDC technique, depending on the operational conditions, gives different particle sizes.[15] It is key to evaluate different particle sizes of sugar since they are used in different applications.











Feed Temp (°C)	Growth rate (µm/h)	Final article size (µm)
55	3.46	44.2 ± 6.79
65	6.57	49.36 ± 9.22
80	9.06	48.9 ± 9.12

Figure 5: Size distribution on particle growth at feed temperatures 80ºC, 65ºC, 55ºC and (a) the growth rate with time and (b) the linearized growth rate.

4. CONCLUSIONS

In the study, synthetic sugar water that was prepared to mimic the sugarcane extract was evaluated in MDC where sugar crystals were simultaneously recovered with high quality water. Peak flux for the 80ºC feed temperature was 0.9 Kg m^{-2} h^{-1} with about 95% recovery factor for the permeated water. The microscopes images were obtained which largely determine the agglomeration process that took place at 80ºC feed temperature. This was further proved by the broad particle size distribution peaks which were more pronounced for the 80ºC feed temperature, the broad peaks indicated dissimilar structures and less uniformity. Also, growth rate was seen to be higher for the 80ºC feed temperature. The study illustrated that MDC technique can be implemented at large industrial scale and hopes to contribute to the development and understanding of MDC technology for sugar production.

5. REFERENCES

1. FAO. FAOSTAT. Available online: http://www.fao.org/faostat/en/#data/QC (accessed on 08 August 2023).

2. Sen, A., & Aggarwal, A. (2017). Comparative Analysis of Sugarcane Production in India and Brazil. International Journal of Current Microbiology and Applied Sciences, 6(6), 2856-2865.

3. De Moura, R. L., Filho, A. G. C., & Cavalett, O. (2019). Sugarcane ethanol as an alternative energy source. Wiley Interdisciplinary Reviews: Energy and Environment, 8(2), e330.

4. K.W. Lawson, D.R. Lloyd, Review: membrane distillation, J. Membr.Sci. 124 (1997) 1– 25.

5. A. Chafidz, S. Al-Zahrani, M.N. Al-Otaibi, C.F. Hoong, T.F. Lai, M. Prabu, Portable and integrated solar-driven desalination system using membrane distillation for arid remote areas in Saudi Arabia, Desalination.345 (2014) 36–49.

6. L. Mart´ınez-D´ıez, F.J. Florido-D´ıaz, Desalination of brines by membrane distillation, Desalination 137 (1-3) (2001) 267–273.

7. M. Tomaszewska, M. Gryta, A.W. Morawski, Recovery of hydrochloric acid from metal pickling solutions by membrane distillation, Sep. Purif. Tech. 22–23 (2001) 591–600.

8. Ali, A., Quist-Jensen, C., Macedonio, F., & Drioli, E. (2015, November 24). Application of Membrane Crystallization for Minerals' Recovery from Produced Water. Membranes, 5(4), 772–792.

9. Singh, R. (2015). Hybrid Membrane Plant Design and Operation. Membrane Technology and Engineering for Water Purification, 283–337.

10. M.N. Chernyshov, G.W. Meindersma, A.B. de Hann, Modelling temperature and salt concentration distribution in membrane distillation feed channel, Desalination 157 (2003) 315–32

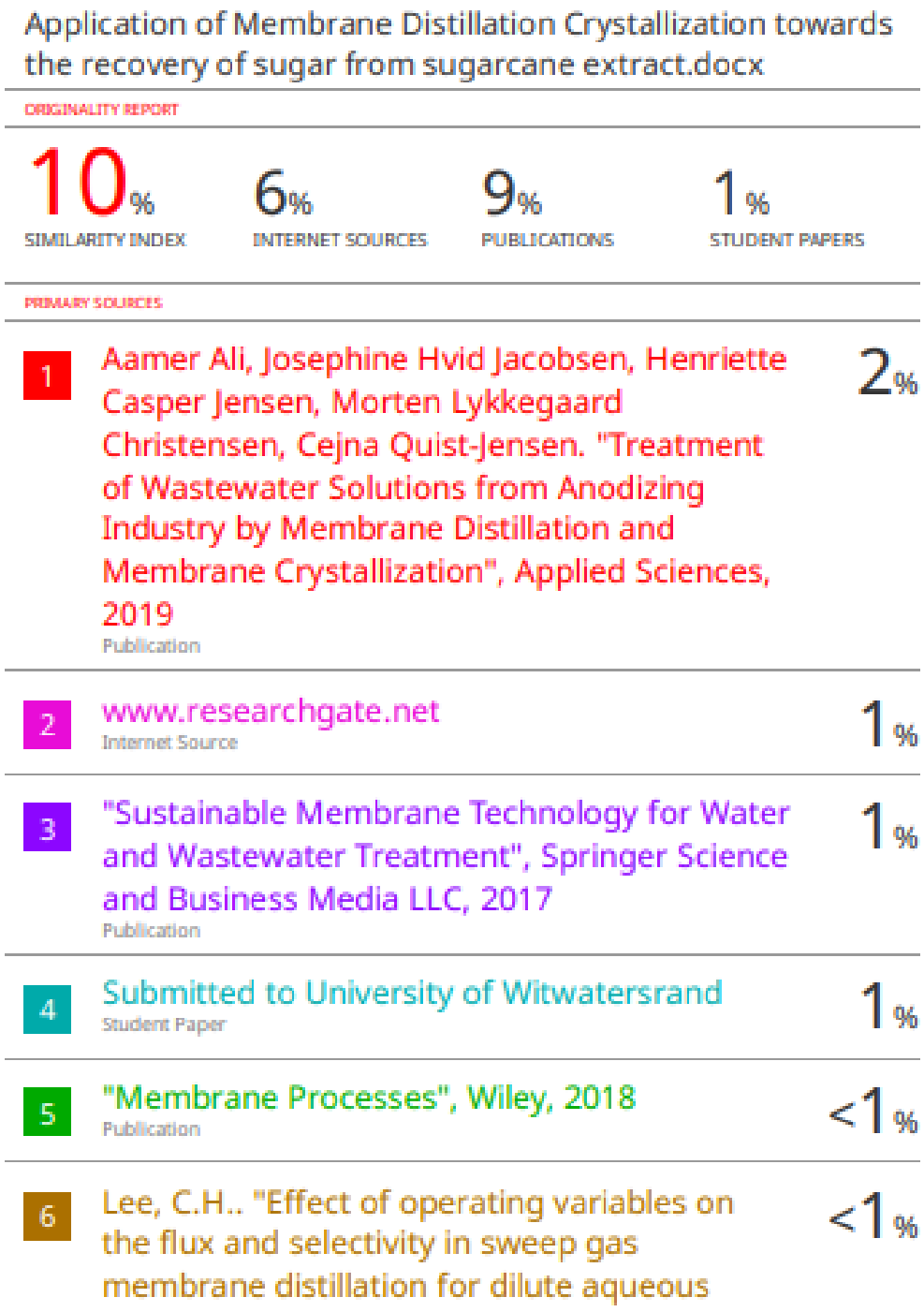
11. Quist-Jensen, C. A.; Macedonio, F.; Drioli, E. Membrane Crystallization for Salts Recovery from Brine—an Experimental and Theoretical Analysis. Desalination and Water Treatment 2015, 57 (16), 7593–7603.

12. R.W. SCHOFIELD, A.G. FANE*, C.J.D. FELL and R. MACOUN Centre for Membrane and Separation Technology, The University of New South Wales, Kensington, N.S.W. 2033 (Australia).

13. Qu, M.; You, S.; Wang, L. Insights into Nucleation and Growth Kinetics in Seeded Vacuum Membrane Distillation Crystallization. Journal of Membrane Science 2020, 118813.

14. Tun, C. M.; Fane, A. G.; Matheickal, J. T.; Sheikholeslami, R. Membrane Distillation Crystallization of Concentrated Salts—Flux and Crystal Formation. Journal of Membrane Science 2005, 257 (1-2), 144–155.

15. B.Y. Shekunov, P. Chattopadhyay, H.H.Y. Tong, A.H.L. Chow, Particle size analysis in pharmaceutics: Principles, methods and applications, Pharm. Res. 24(2007) 203–227.



Application of Membrane Distillation Crystallization towards the recovery of sugar from sugarcane extract.docx

ORIGINALITY REPORT

10%	6%	9%	1%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Aamer Ali, Josephine Hvid Jacobsen, Henriette Casper Jensen, Morten Lykkegaard Christensen, Cejna Quist-Jensen. "Treatment of Wastewater Solutions from Anodizing Industry by Membrane Distillation and Membrane Crystallization", Applied Sciences, 2019 Publication	2%
2	www.researchgate.net Internet Source	1%
3	"Sustainable Membrane Technology for Water and Wastewater Treatment", Springer Science and Business Media LLC, 2017 Publication	1%
4	Submitted to University of Witwatersrand Student Paper	1%
5	"Membrane Processes", Wiley, 2018 Publication	<1%
6	Lee, C.H.. "Effect of operating variables on the flux and selectivity in sweep gas membrane distillation for dilute aqueous	<1%