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Integration of Membrane Processes for Decolourization of Starch Hydrolysates

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The decolourization during the production of starch hydrolysates involves removing impurities to obtain a brilliant, light-coloured, transparent syrup. However, conventional processes in the industry result in low yield and quality, wasting energy and high-value chemicals. Therefore, starch hydrolysate production requires new separation techniques, such as membrane separation technology, which have overcome traditional methods in different applications. This technology used for product decolourization can reduce chemicals and benefit the subsequent evaporation and crystallization processes, increasing product recovery. Nevertheless, a single membrane step is sometimes impractical in achieving high colour removal, desalination, and sugar permeation due to their limited selectivity in complex solutions and low permeate flux. Consequently, integrating different membrane processes is necessary to improve separation selectivity and decolourization while ensuring high operational flux. In this study, three commercially available membranes (70 kDa, 5 kDa and 150-300 Da) were selected to investigate the colour removal, sugar permeation and conductivity change from a diluted glucose syrup obtained from saccharified starch hydrolysates. The experiments were conducted with a lab-scale crossflow membrane module and constant temperature (60°C). Depending on the maximum capacity of each membrane unit, different operating conditions were considered (feed concentration and transmembrane pressure). The most colour removed was achieved with the 5 kDa membrane with 36 %, followed by the 70 kDa membrane with 27.5 %. Besides, a considerable portion of salts can be removed during NF or 150-300 Da membrane, with an approximated 56 % conductivity change. This study proposed an integrated membrane system and using a theoretical balance was found that the colour of starch hydrolysates could be reduced to 53.6 % using three different steps of membrane filtration. These results will be helpful in the future as a starting point to evaluate in more detail the integration of varying membrane separation techniques and possible process scale-up. The new integrated system is expected to improve the separation of non-sugar compounds and operating conditions during starch hydrolysates' decolourization.

1. Introduction

Starch hydrolysates production has high-quality target products where low content of colour is often required with a high range of reducing sugars. This product is an essential source of many necessary substances for human consumption like food ingredients, health care products, pharmaceutical products, and other applications. Despite their various applications, starch hydrolysates (dextrin, syrups) are extensively used in the food industry, and their degree of polymerisation is an essential analytical characteristic (Stephen and Merrifield, 2005). The hydrolysates provide sweetness, softness and shine to the food but also decrease water and microbiology activity extending the product's shelf life besides other benefits (Acevedo-Estupiñan et al., 2015). Numerous technologies are available to remove colour or recover pigments, such as activated carbon (AC), chitosan adsorbents, ion exchange resin adsorption, chemical and biological reactions, extractions, etc. However, these technologies require absorbent pre-treatment and regeneration needing more chemicals for the methods that can also induce environmental and safety problems (Guo et al., 2019). Membrane operations like Ultrafiltration (UF) and Nanofiltration (NF) contribute to a green perspective to recover starch hydrolysates. They

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have been widely applied in the colour removal of sugarcane juice, fermentation broth, wastewater, palm oil production and others as a simpler, straightforward method than the conventional process, with a small footprint, no need for chemicals, and usually with mild operating parameters (Ambrosi et al., 2014).
Like other food industry products (sugarcane juice), the starch hydrolysates production call for an equilibrium between colour removal and reducing sugar permeability (Luo et al., 2016). However, a single membrane or filtration process is impractical in achieving high colour removal efficiency and sugar permeation due to their limited selectivity in complex solutions, low permeate fluxes and membrane fouling (Hamachi et al., 2003). These technical problems hamper this technological upgrading on an industrial scale. Consequently, to make this technology more viable for the decolourisation of starch hydrolysates, more research is needed to improve membrane selection and integration processes to increase the residual sugar recovery, reduce the fouling mechanisms, and enhance a better membrane cleaning.
This study proposes an integrated membrane system to decolourise and purify starch hydrolysates with satisfactory permeate fluxes. Three commercially available UF and NF membranes were evaluated individually, and membrane crossflow tests were used under similar operating conditions to analyse the behaviour of each membrane in the proposed multistage process. Figure 1 shows the filtration process that was considered in this investigation; a loose UF (with a pore size of 70 kDa) is applied to remove large pigments in the glucose syrup, and a tight UF (with a pore size of 5 kDa) is applied to decolourise the clarified juice further. Then, NF (with a pore size of around 150-300 Da) is used to concentrate the final UF permeate and reduce the content of salts. The crossflow test conditions considered the possible operating conditions entering each system and the capacity of each membrane (feed concentrations, temperature, pressures, etc.). The outcome of this work provides an idea of the benefits of decolourisation, sugar permeation and demineralisation of the final syrup by a multistage membrane process. It guides novel membrane developments and process design in the industrial production of starch hydrolysates.

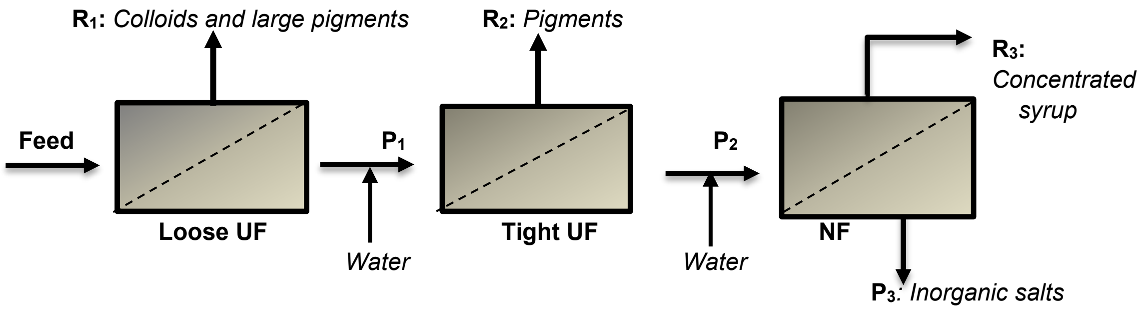

Figure 1: Diagram of decolourization of starch hydrolysates by an integrated membrane system (R=Retentate; P=Permeate).

2. Materials and methods

2.1 Feed syrup

AGRANA Stärke GmbH (an Austrian starch processing company) provided prefiltered starch hydrolysates without colloids and suspended matter. These starch hydrolysates are in the form of glucose syrup prepared by enzymatic hydrolysis of maize and wheat with specific properties and is a liquid, highly viscous solution with high glucose concentrations. The provided syrup was diluted with Milli-Q water before filtration to dry solid content of 30 % (in the called feed), 20 % (in the called P_1) and 1 % (in the called P_2). These concentrations were selected based on previous trials where the permeate coming out of the loose UF was around 28 % DS, the permeate coming out of the tight UF was about 18 %DS, and the final permeate of the NF was approximately 0.8 %DS with all the final product in the retentate with around 21 %DS. Therefore, feed syrup was diluted for each membrane as appropriate to improve flux, especially for tight UF and NF membranes. In addition, a standard pH value of around 4.5 was selected to yield comparable results considering different possible saccharification products and improve the syrup's colour stability, especially at the high temperature chosen. The pH was adjusted if needed by adding low quantities of H2SO4 and NaOH, so minimal changes in the content of salts were observed.

2.2 Equipment and membranes

A Lab-scale filtration membrane unit model OS-MC-01 was used for the experiment. This membrane unit consists of a two-litre feed tank with a stainless-steel jacket and a flat sheet membrane module with an effective area of 0.008 m^2 (0.04m x 0.2m). A Piston Pump (CAT pump; model-231) is supplied from the 2 L feed tank and pushes the bypass and the membrane’s fluid. The unit has a maximum flow capacity of 3.7 L min^{-1} and a maximum pressure of up to 64 bar. The trials were performed in batch mode, where the retentate was recycled back to the feed tank while the permeate was continuously collected in a vessel located on a digital balance to measure the permeate flux through the process. At the end of each batch, around 500 mL is collected as retentate, and 1500 mL is collected as permeate, the recovery is about 75 %. Additionally, the feed tank is equipped with a heating unit (VWR) to heat the liquid to the desired temperature. The equipment can operate at a temperature ranging from 5 °C to 70 °C. The schema of the Lab-scale filtration unit can be found in the recent article by Cabrera-González et al. (2022). Table 1 shows the selected three flat sheet membranes considering the type of membrane (loose UF, tight UF and NF), the different molecular weight cut-off (MWCO) and their resistance to high temperatures or near the hydrolysis temperature to avoid microbiological fouling on the membrane.

Table 1: Main properties of the polymeric membranes

Parameter	Loose UF	Tight UF	Tight NF
MWCO (kg mol^{-1})	70	5	0.15 – 0.3
Operating temperature range (°C)	5 - 60	60	80
Operating pH range	2 – 10	2 – 10	2 – 10
Typical operating pressure (bar)	2.1 – 8.3	2.1 – 8.3	40

2.3 Conditions during filtration

Depending on the filtration type and considering the multistage filtration proposed, different concentrations in the initial syrup were used, as mentioned in section 2.1. The filtration process was kept at similar conditions with a temperature of 60°C, which allowed to it work close to hydrolysis temperature, under conditions of continuous production and avoiding microbiological fouling on the membranes. Loose and tight UF were operated at a Transmembrane Pressure (TMP) of 8 bars, while the NF was performed at a TMP of 30 bars, the pressure was selected according to the maximum capacity of the membranes. After each trial, the effect of different variables was evaluated, such as decolourization, sugar rejection, and conductivity change, together with the permeate flux to estimate membrane performance in the multistage system. The different variables considered during the operating experiments are in Table 2. Brix, permeate flux, pH and conductivity were measured continuously until the end of the filtration to observe each membrane's behaviour through the time.

Table 2: Operating conditions

Parameter	Loose UF	Tight UF	NF
Temperature (°C)	60	60	60
Transmembrane Pressure (bar)	8	8	30
Feed Concentration (°Brix)	30	20	15

2.4 Analytic methods

A UV/visible scanning spectrophotometer (UV-1800 Shimadzu) was used to determine the colour in the feed, permeate and retentate based on ICUMSA Method GS2/3-10, which is a spectrophotometric method at 240 used in sugar analysis(Giani, 2018). Therefore, the colour is given in ICUMSA units (IU, international units for sugar colour). Brix measurements were used to estimate the sugar concentration on the samples; therefore, the sugar concentrations were evaluated using an Optronic Digital Refractometer (KRÜSS DR6200-T) to measure the index refraction at a temperature of 20°C. Brix values are used to measure the refractometric dry substance in an aqueous solution, namely the amounts of dissolved solids per weight of the total solution (Elewa et al., 2020). The pH and conductivity values were measured in the feed, permeate and retentate using a digital pH meter (PH-100 ATC Voltcraft) and a digital conductivity meter (WA-100 ATC Voltcraft). The conductivity values were used to estimate the salts' removal during the tests; the conductivity helps as a quick test to determine if there is a migration of ions from the feed tank to the permeate through the membrane (Cabrera-González et al., 2022). To evaluate the fouling of each test, the water permeability of membrane modules was measured before and after feed filtration and cleaning, respectively. Finally, colour rejection, sugar retention and conductivity change were calculated with the following Eq(1), determining the performance of each stage process. Where C_p, C_f is the concentration (sugar), absorbance (pigment), or conductivity (ions) of the permeate and feed.

$$R = \left(1 - \frac{C_p}{(C_f)}\right) * 100\,\% \qquad (1)$$

3. Results and Discussions

3.1 Membrane Separation Performance

Considering the initial composition of the syrup, the glucose syrup still contains a few impurities, such as colloids, pigments, and inorganic salts. The presence of colloids, pigments and suspended solids impact membrane fouling on the membrane surface and in the flow channels of the membranes (Merino-Garcia and Velizarov, 2021). For this reason, a loose UF membrane was selected in the first stage of the process due to the high MWCO and large flow channels to remove the main foulants at the beginning of the system and enables a high crossflow velocity (strong antifouling performance). After loose UF treatment, no flux reduction occurred considering the water permeability of the membrane before and after feed filtration. In this case, it can be assumed that there is no considerable effect on the surface of the membrane from the filtration of the glucose syrup (Shi et al., 2019). On the other hand, the sugar content and the conductivity did not change significantly, with only 3 % sugar retention and 1.5 % conductivity change. At the same time, 27.5 % of colour was removed from 2597 to 1882 IU. This colour removal indicates that high molecular weight (HMW) pigments and a portion of colloids and suspended solids could be removed by loose UF. The resulting permeate could be further treated by a tight UF membrane with smaller MWCO and lower antifouling performance to remove more pigments in the syrup (Luo et al., 2016).

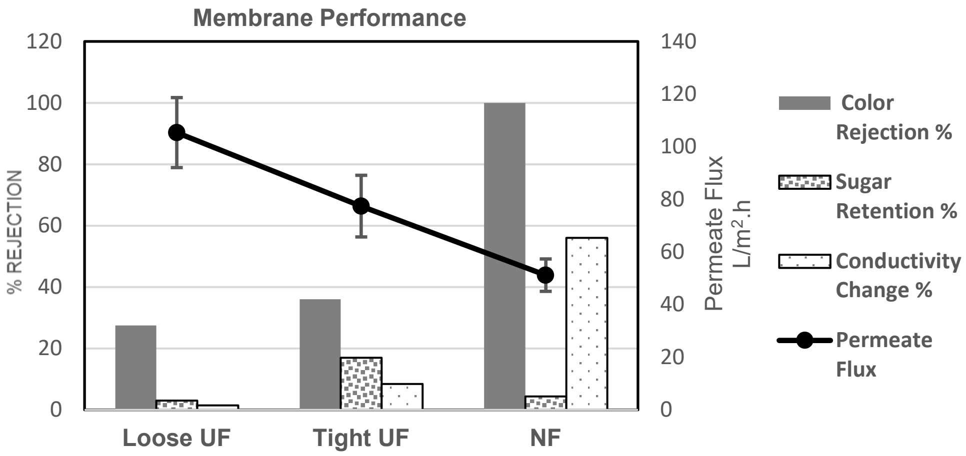

Figure 2: Performance of the membranes during filtration (Colour removal, Sugar permeability and Salt rejection) Operating parameters: 60 °C, 3.6 L/min, 8 bar for UF and 30 bar for NF. Permeate flux - Volume of permeate recollected during membrane separation per unit of time and membrane area.

After analysing the loose UF, the same feed syrup was used but at a lower concentration to determine the behaviour of the tight UF in the proposed system. The concentration in the permeate leaving the loose UF is expected to be around 28 %DS considering the first test, so dilution of the glucose syrup until 20 %DS with deionised water was necessary to continue with the tight UF analysis. This dilution was used to improve flux and reduce the risk of fouling. However, after tight UF, the water flux permeability diminished by 30% even when the membrane presented good average permeate fluxes indicating fouling growing on the surface of the membrane after the filtration of the glucose syrup. This membrane experienced the most flux reduction confirming that a previous loose UF step could be beneficial in reducing the fouling formation (Luo et al., 2016). However, it is noticed that the tight UF retain sugars, with around 17 % sugar loss leading to low sugar productivity in the following stages. In this case, the recovery of these sugars could be facilitated by recycling the retentate, a new diafiltration mode, or an additional colour removal method (Mudoga et al., 2008).

Finally, the NF stage was studied to concentrate the light-coloured syrup in the proposed system and demineralise the final product. In this case, the final product comes from the retentate, not the permeate. The concentration exiting the tight UF stage is around 18 %DS, so the addition of deionised water in the feed syrup until 15% DS was made during the NF stage. As expected, the NF permeate is clear and colourless, and the total sugar concentration in the permeate is only about 0.8 %DS, with a sugar loss of only 4.4 %. On the other hand, a considerable portion of salts is removed, with an estimated 56% passing through the NF membrane to the permeate. This confirms the advantages of having an NF step in the system, retaining only multivalent ions and organic solutes with molecular weights above 300 Da while significantly allowing monovalent ions' passage and removing a certain amount of salts in the solution (Samee et al., 2016). Previous studies have also confirmed the effects of tight NF in the concentration and desalination of molasses as an effective complementary technology (Luo et al., 2019). Surprisingly, another important benefit of the NF membrane in this study is the low fouling effect, with only 4.6% flux reduction after filtration.

The filtration velocity and permeate fluxes depend on the type of membrane used and MWCO, as observed in Figure 2. The nature of the membrane surface and the tangential velocities are different in all the membranes studied. As expected, the membrane with the highest MWCO or loose UF membrane obtained the highest permeate flux with a value of 105.4 ± 13.3 L/m^2.h, followed by the tight UF membrane with a value of 77.4 ± 11.7 L/m^2.h, and finally, the membrane with the lowest MWCO or NF membrane had the lowest permeate flux with 51.2 ± 6.2 L/m^2.h. In other words, as the flow advances in the proposed system, the crossflow velocity also could decrease. In general, the permeate fluxes in this investigation are not critical in any of the stages, possibly due to the high temperature used, which made the permeate fluxes acceptable for the system because of the lower syrup viscosity (Mudoga et al., 2008). At the same time, the higher diffusion and the larger defective pore diameter of the membranes could also cause a reduction in the retention percentages, which could explain the sugar loss during the tight UF stage (Tsuru et al., 2000).

3.2 Benefits of the membrane Process Integration

The process integration was proposed to exploit the performance of each type of membrane mentioned in section 3.1 and overcome the limited membrane selectivity in the treatment of the complex starch hydrolysates. A better decolourization of the glucose syrup and the removal of salts are expected. Considering the initial composition of the starch hydrolysates and the removal percentages obtained previously, a theoretical mass balance across the filtration process is provided in Table 3 to estimate the total removal percentages in the integrated membrane process.

Table 3: Mass balance across the integrated membrane system

Index	Feed syrup	Loose UF P_1	Tight UF P_2	NF R_3	Total % Rejection
Colour (IU/420 nm)	2,597	1,882.8	1,204.9	1,204.9	53.6%
Brix (% DS)	30	29.1	24.2	2.1	23%
Conductivity (µS)	700	689.5	630.9	278.1	60.3%

Table 3 shows that the improvement of the final product could be possible with an integrated membrane system. The final product from the NF retentate increases its purity with 53.6 % of total colour removal and 60.3% demineralisation. The colour value in the final product is 1,204.9 IU, two times lower than the initial value. Due to the superior product quality compared to a single membrane process, the integrated membrane process (Two-stage UF followed by NF) could replace the conventional methods for decolouration of starch hydrolysates. However, the total sugar loss of the system is considerable at around 23 %. To improve the economic benefits of this system, recovery of residual sugar in UF retentate by diafiltration, or other recovery methods is recommended to be studied together with a more detailed analysis of the multistage process.

4. Conclusion

The combination of UF and NF processes can improve the decolourization and demineralization of starch hydrolysates. By the integrated membrane process, the final colour removal and demineralization were around 53.6% and 60%. In addition, it can be concluded that the use of high temperatures accelerates the sugar permeation across the membrane, attenuating the concentration polarisation layer and intensifying the sucrose retention to around 23 % induced by high permeate fluxes. The most significant sugar loss was obtained during the tight UF process. However, sugar recovery should be investigated by diafiltration or other recovery methods in the following studies to further improve the system's benefits.

Additionally, a more detailed analysis of the multistage membrane system proposed here is needed to assess the fouling mechanisms, the best operating parameters, and the enhancement of a better membrane cleaning. In general, membrane fouling is a big challenge in starch hydrolysates decolourization; however, an integrated membrane can attenuate the fouling and its promise to be quickly industrialized. The loose UF step could break up the first foulants (suspended solids, colloids, and big pigments), while the tight UF other secondary fouling (small pigments) avoid fouling aggravation in the following steps like NF. In addition, if a more efficient performance of the membranes is achieved during the integrated process, including better permeate fluxes, the reduction of the membrane area for the process could also be achieved.

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References

Acevedo-Estupiñan, M. V, Parra-Escudero C. O., Muvdi-Nova C. J., 2015, Study of clarification process of cassava starch hydrolysates using ceramic membranes, Vitae, 22(2), 121–129.

Ambrosi A., Cardozo N., Tessaro I., 2014, Membrane Separation Processes for the Beer Industry: A Review and State of the Art, Food and Bioprocess Technology, 7(4), 921–936.

Cabrera-González M., Ahmed A., Maamo K., Salem M., Jordan C., Harasek M., 2022, Evaluation of Nanofiltration Membranes for Pure Lactic Acid Permeability, Membranes, 12, 302.

Dziedzic S. Z., Kearsley M. W., 1995, Handbook of Starch Hydrolysis Products and Their Derivatives, Springer New York, NY.

Elewa M., El-Saady G., Ibrahim K., Tawfek M., Elhossieny H., 2020, A novel Method for Brix Measuring in raw Sugar Solution, Egyptian Sugar Journal, 15, 69–86.

Giani S., 2018, Determination of Sugar Solutions Color According to ICUMSA / Application Note Analytical Chemistry, Chapter 10, 189–225.

Guo S., Luo J., Yang Q., Qiang X., Feng S., Wan Y., 2019, Decoloration of Molasses by Ultrafiltration and Nanofiltration: Unraveling the Mechanisms of High Sucrose Retention, Food and Bioprocess Technology, 12, 302.

Hamachi M., Gupta B. B., Ben Aim R., 2003, Ultrafiltration: A means for decolorization of cane sugar solution, Separation and Purification Technology, 30(3), 229–239.

Luo J., Guo S., Qiang X., Hang X., Chen X., Wan Y., 2019, Sustainable utilization of cane molasses by an integrated separation process: Interplay between adsorption and nanofiltration, Separation and Purification Technology, 219, 16–24.

Luo J., Hang X., Zhai W., Qi B., Song W., Chen X., Wan Y., 2016, Refining sugarcane juice by an integrated membrane process: Filtration behavior of polymeric membrane at high temperature, Journal of Membrane Science, 509, 105–115.

Merino-Garcia I., Velizarov S., 2021, New insights into the definition of membrane cleaning strategies to diminish the fouling impact in ion exchange membrane separation processes, Separation and Purification Technology, 277, 119445.

Mudoga H. L., Yucel H., Kincal N. S., 2008, Decolorization of sugar syrups using commercial and sugar beet pulp based activated carbons, Bioresource Technology, 99(9), 3528–3533.

Samee M. A., Elgohary A. A., Harasek M., Friedl A., 2016, Experimental investigation of nanofiltration process for the separation of complex sugar mixtures containing mono- and multivalent salts, Chemical Engineering Transactions, 52, 799–804.

Shi C., Rackemann D. W., Moghaddam L., Wei B., Li K., Lu H., Xie C., Hang F., Doherty W. O. S., 2019, Ceramic membrane filtration of factory sugarcane juice: Effect of pretreatment on permeate flux, juice quality and fouling, Journal of Food Engineering, 243, 101–113.

Stephen A. M., Merrifield E. H., 2005, Carbohydrates, Overview, Worsfold P., Townshend A., Poole C., Miro M., Encyclopedia of Analytical Science, Second Edition, Oxford, UK, 392–408.

Tsuru T., Izumi S., Yoshioka T., Asaeda M., 2000, Temperature effect on transport performance by inorganic nanofiltration membranes, AIChE Journal, 46(3), 565–574.