CHEMICAL ENGINEERING TRANSACTIONS
VOL. 96, 2022

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: David Bogle, Flavio Manenti, Piero Salatino

ISBN 978-88-95608-95-2; **ISSN** 2283-9216
DOI: 10.3303/CET2296012

Sustainable Industrial Treatment of Starch Hydrolysates

Camila A. Cabeza[a,b]*, Amal El-Gohary-Ahmed [a], Mario Minauf [c], Michael Harasek[a]

[a] Institute of Chemical Environmental & Bioscience Engineering E166, Technische Universität Wien, 1060 Vienna, Austria.
[b] Competence Center CHASE GmbH, Ghegastraße 3 Top 3.2, 1030 Vienna, Austria
[c] AGRANA Research & Innovation Center GmbH, Josef-Reither-Strasse 21-23, 3430 Tulln, Austria
camila.cabeza@tuwien.ac.at

Starch hydrolysates have strict quality demands of production where low content of impurities is required. The quality of the product depends on the raw material, the suitability of clarification and the evaporation process of juices. The manufacture of starch products plays an essential role in numerous applications in widely different industries, such as food ingredients, cosmetics, pharmaceutical products, and other products for wide-ranging technical applications. However, the current industrial downstream processes used after hydrolysation to purify these products significantly impact the environment and have high energy demands. For this reason, it is essential to investigate other sustainable separation techniques commercially available for the industry, such as membrane separation technologies. Membrane technology could increment the quality of the product while reducing energy consumption and waste production compared with other methods. For instance, ultrafiltration (UF) membranes have demonstrated the efficient separation and purification of various sugar juices. They are pressure-driven membranes able to fractionate the product from non-sugar compounds and impurities. Therefore, as a starting point, this research evaluated two different UF membranes available in the market to treat starch hydrolysates (70 kDa and 20 kDa). The influence of two operating parameters, such as temperature and transmembrane pressure (TMP), on the separation of colour particles, sugar permeation and permeate flux from the starch hydrolysates were evaluated through the filtration processes. The 70 kDa membrane obtained the best performance at optimal operating conditions of 60 °C and 8 bar with around 27 % colour removal, the highest permeate flux value of 105.4 L/m^2.h and minimum sugar loss of 3%. Finally, the results indicate the suitability of UF technology for the partial decolourisation of starch hydrolysates; however, it is recommended to continue studying the combination of UF with another separation method to eliminate the remaining impurities in the final product. These results would be a valuable guide for downstream process design and practical operation in subsequent industrial applications.

1. Introduction

The raw materials to produce starch hydrolysates are polysaccharides made up of glucose units (Acevedo-Estupiñan et al., 2015). Starch hydrolysates are presented in the form of glucose syrups, which are liquid solutions highly viscous with high glucose concentrations of around 75 %DS (Singh & Cheryan, 1998). These glucose syrups have different sweetening power; being the 100 Dextrose Equivalents (DE) the sweetest power of sucrose (Hobbs, 2009). Despite their different applications, these syrups are highly appreciated in the food industry since they provide sweetness, softness, and shine to the products, besides their capacity to decrease water activity, prolonging the product's duration among other benefits (Acevedo-Estupiñan et al., 2015). Therefore, this final product could be used in products like chocolates, ice creams, and sweets in general (Dziedzic & Kearsley, 1995).
The starch hydrolysation results in a deterioration of the product and a reduction of the length of the molecules to transform dextrin into low molecular weight sugars, such as glucose, maltotriose, maltose or mixtures (Dziedzic & Kearsley, 1995). This process led to the further forming of colour molecules and the introduction of impurities like non-sugar compounds as salts and proteins into the glucose syrup, obtaining a product with a determined sugar composition but with a considerable colour content (Shahidi Noghabi & Razavi, 2015). Different colour compounds are formed during this stage by polymerization, polycondensation, disintegration or

Paper Received: 17 January 2022; Revised: 16 June 2022; Accepted: 5 September 2022
Please cite this article as: Cabeza C.A., El-Gohary-Ahmed A., Minauf M., Harasek M., 2022, Sustainable Industrial Treatment of Starch Hydrolysates, Chemical Engineering Transactions, 96, 67-72 DOI:10.3303/CET2296012

caramelization. An example of these non-sugar compounds are the colour particles called the Melanoidins which are compounds generated in the late stages of the Maillard reactions from reducing sugars and proteins, peptides or amino acids during the food processing and preservation (Wang et al., 2011). Therefore, starch hydrolysates are normally filtered using different methods like Activated Carbon (AC) and Ion Exchange (IE) technology to remove the colour, flavour, and other smaller particles (Hobbs, 2009). Consequently, it is concentrated through the evaporation process to around 70 %DS (Hernández-Uribe et al., 2008). Nevertheless, the conventional downstream technologies used in the industry results in long processes to achieve optimum product, low yield and quality, high costs by wasting both energy and high-value chemicals, without mention the significant impact in the environment and high energy demands (Bhattacharya et al., 2001). Accordingly, starch hydrolysates production requires finding and investigating new separation techniques, such as membrane processes, which have already excellent prospects and have overcome traditional methods (Guo et al., 2019).
Starch hydrolysates processing requires low content of non-sugar impurities, including pigments, with high content of sugars (Gyura et al., 2002). Therefore, clarification and decolourisation steps are the second main responsible for batch production, obtaining a brilliant, light coloured and transparent syrup (Luo et al., 2016). Membrane processes in different industries have already been analysed, and their benefits have been proved over time (Cassano & Drioli, 2014). This technology, readily available on an industrial scale, helps with product decolourisation and could eliminate chemicals and bring different benefits, including during the evaporation and crystallisation steps, by decreasing energy consumption and increasing sugar recovery (Benkun Qi et al., 2017). Besides membrane technology could replace or complement other conventional technologies like the mentioned IE, and the AC allowing obtaining a quality product in terms of turbidity, colour, and microbiological content (Acevedo-Estupiñan et al., 2015).
This research investigated the potential of ultrafiltration (UF) for the decolourisation of starch hydrolysates. Two commercially available UF membranes were tested on a lab-scale crossflow membrane module under different operating conditions to evaluate the influence of temperature and TMP on the average permeate flux, colour, and sugar rejection. These results are a first overview to choose the best membrane performance and operating conditions for the future design of downstream processes for starch hydrolysates treatment.

2. Materials and Methods

2.1 Feed Solution

Glucose syrup from starch hydrolysates is provided by AGRANA Stärke GmbH (an Austrian starch processing company) at a high concentration of reducing sugars of around 70 %DS. It was obtained mainly from maize and wheat starch by an enzymatic hydrolysis process. First, the glucose syrup was diluted at room temperature with deionized water until a homogeneous solution of around 30 °Brix. Since there may be a deviation in the native pH value of the different saccharification products, a standard pH value of around 4.5 was selected to yield comparable results. This value has improved colour stability of the syrup, especially at higher filtration temperatures. The pH of the initial solution was adjusted if needed by adding low quantities of H_2SO_4 and NaOH.

Table 1:Characteristics of the membranes

Parameter	Membrane I	Membrane II
MWCO (kg mol^{-1})	70	20
Max Operating temperature (°C)	60	75
Operating pH range	2 – 10	2 – 10
Max operating pressure (bar)	8	9

2.2 Experimental Set-Up and Membranes

Lab-scale crossflow filtration membrane unit was used for the experiments, model OS-MC-01, consisting of a flat sheet membrane module with an effective membrane area of 0.008 m^2 (0.04m x 0.2m). The schema of the membrane test cell can be found in this article (Cabrera-González et al., 2022). The membrane unit comprises a two-litre feed tank with a stainless-steel jacket. The feed syrup is pumped to the rectangular membrane module through a high-pressure piston pump (CAT pump; model-231). The unit has a flow capacity of 3.7 L min^{-1} and a maximum pressure of up to 64 bar. All the trials were performed in batch mode, where the retentate was recycled back to the feed tank. At the same time, the permeate was continuously collected in a vessel located on a digital balance to measure the permeate flux through the process. Additionally, the feed tank is equipped with a heating unit (VWR) to heat the liquid to the desired temperature. Two flat sheets of UF polymeric

membranes were selected considering different molecular weight cut-off (MWCO), and operating pressures and temperatures (
). They can be used to process food at hydrolysis temperature conditions to avoid microbiological fouling on the membranes.

2.3 Experimental Conditions

The filtration processes evaluated two independent variables to determine their effect on colour removal, sugar retention, and average permeate flux. A factorial design is applied where the impacts of temperature and transmembrane pressure were considered at two levels (high and low values) while maintaining the same feed concentration (30 °Brix). The different independent variables considered are represented in *Table 2*. Brix, permeate flux, pH and conductivity were measured until a certain amount of permeate was collected (~1400 mL).

Table 2: Boundaries of independent variables

Parameter	Lower	Upper
Temperature (°C)	40	60
Transmembrane Pressure (bar)	2	8

2.4 Analytic Methods

A UV/visible scanning spectrophotometer (UV-1800 Shimadzu) was used to determine the colour in the feed, permeates and retentates according to an ICUMSA spectrophotometrically method (GS2/3-10) at 420 nm 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 using a digital pH meter (PH-100 ATC Voltcraft) and a digital conductivity meter (WA-100 ATC Voltcraft). 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 and sugar permeability were calculated with the following Eq (1) determining the performance of each stage process. Where C_p, C_f are the concentration (sugar) or absorbance (pigment), of the permeate and feed.

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

3. Results and Discussion

The performance of UF membranes on decolourization and sugar permeability was investigated considering different operating conditions. The term decolourization in this work refers to removing natural pigment existing in the glucose syrup obtained from saccharified starch hydrolysates, and the permeability concept refers to the accumulated amount of reducing sugars in the permeate side. The main objective of the UF was to obtain colour rejection and sugar permeability, which means that the final product results from the permeate line and must have high sugar with lower colour content.

3.1 UF membrane performance

The UF results show that the filtration fluxes depend on the type of membrane used, its material, and its MWCO. Although the effects of temperature and pressure can be compared during all the experiments, the nature of the flow along the membrane surface and tangential velocities are different in both UF membranes studied. Membrane I with large MWCO (70kDa) obtained the highest permeate flux value during the filtration process, with 105 $L/m^2.h$, than membrane II with lower MWCO (20kDa) with 35 $L/m^2.h$. High permeate flux is beneficial because it alleviates the concentration polarisation layer in the membrane surface, which increases the transport of solutes like reducing sugars across the membrane into the permeate, decreases membrane fouling, and increases sugar recovery during the process. However, high permeate flux sometimes can also provoke the dilution of some other solutes across the membrane (concentration polarisation effect), which increases the solute rejection decreasing, for example in this case, the colour permeation (Guo et al., 2019).

Both UF membranes had similar behaviour regarding the decolourisation of starch hydrolysates with around 35 % highest colour rejection value. This behaviour could mean that approximately 35 % are large colour particles above 70 -20 kDa, while the other 70% are smaller colour particles below 20 kDa. Nevertheless, membrane I represented the best sugar permeability under the best conditions, with a slight sugar loss of 3 % due to its large pore size. In comparison, membrane II had a considerable sugar loss of around 17 %. The high permeate fluxes observed in membrane I, especially at high temperature and TMP, had a low concentration polarisation effect during sugar permeation, where the reducing sugars were transported across the membrane into the permeate. However, this membrane still positively impacted colour removal due to a dilution effect where the colour particles were diluted across the membrane surface, with similar removal values to the lower MWCO (20 kDa) membrane.

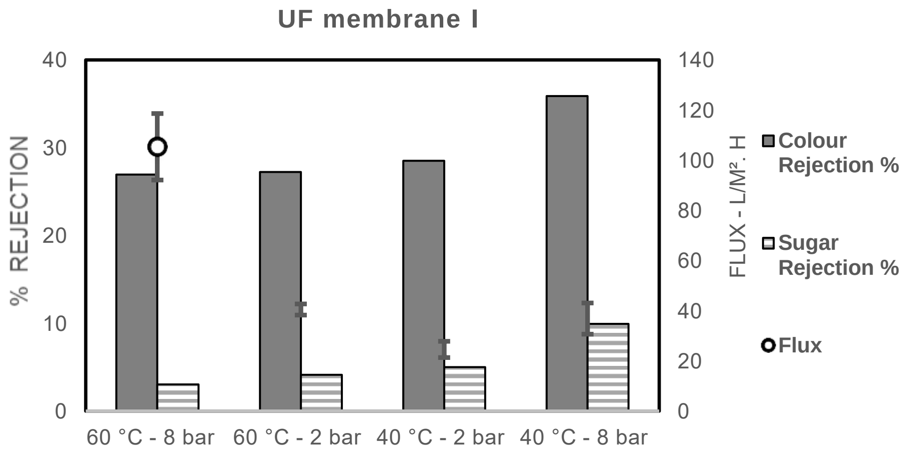

Figure 1: Influence of operating parameters in decolourisation, sugar permeability and flux (70kDa membrane)

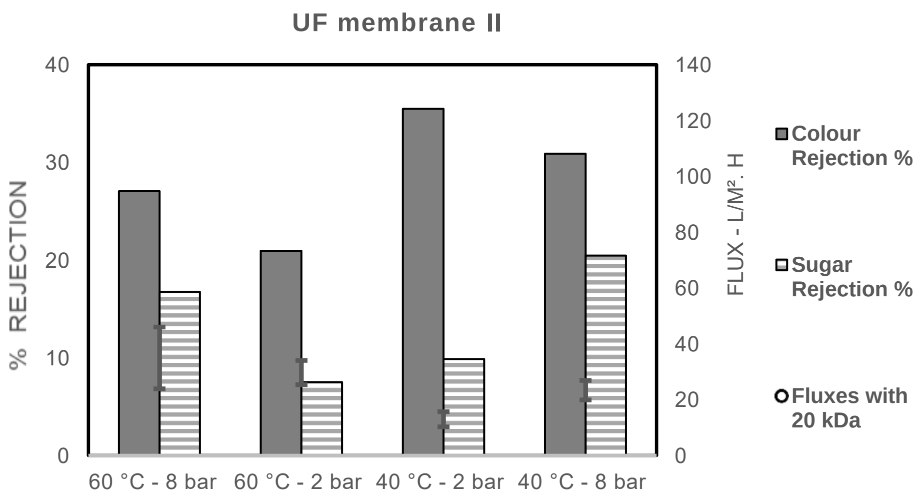

Figure 2: Influence of operating parameters in decolourisation, sugar permeability and flux (20kDa membrane)

On the other hand, membrane II had a significant membrane fouling with a value of around 31% flux reduction considering the water permeability of the membrane before and after feed filtration. Membrane fouling also decreased sugar recovery from 7 to 20 % since foulants block and narrow the membrane pores, especially when a lower MWCO is available, increasing solute rejection due to the called membrane fouling effect (B Qi et al., 2017). Whereas during filtration with membrane I, no flux reduction occurred, assuming that there is no considerable membrane fouling effect on the surface of the membrane during the filtration of starch hydrolysates (Shi et al., 2019). Therefore, lower sugar loss is also observed.

3.2 Influence of operating conditions

The influence of operating conditions on each UF membrane's rejection percentages and fluxes is summarised in Figures 1 and 2. At low temperature, the highest colour removal is observed in both membranes. However, at low temperature, the viscosity is also high, which decreases the sugar permeation through the membrane incrementing the sugar loss in the processes. Although low temperatures could benefit better colour removal during UF, they could harm the process by increasing sugar loss and fouling phenomena. Moreover, the lower temperature reduces the permeate flux in the system, resulting in larger membrane areas to receive enough flow for the industrial application. Therefore, the overall performance improved with increasing temperature, especially in membrane I, which obtained the best general performance leading to a higher permeate flux. This fact may be attributed to the decrease in feed viscosity and the increase in diffusivity (Alventosa-De Lara et al., 2012). Due to the lower viscosity, the transport of reducing sugars through the membrane intensifies, yielding a higher permeate flux where the permeate volume per unit of time and membrane area is higher when the temperature increases. Therefore, this also explains why membrane I had no flux reduction and fouling effect.
Besides, in membrane I is observed that TMP significantly affects colour removal and sugar loss at low temperature. At the same time, high pressure does not substantially affect it at high temperature, also improving the permeate fluxes in the system. This effect can be attributed to the higher driving force in the system; thus, the average permeates flux and sugar permeation obtained is more significant as pressure and temperature increase (Alventosa-De Lara et al., 2012). In this case, the rejection coefficient decreased by increasing TMP due to the passage of sugar molecules through the membrane under increased TMP, which ultimately increased sugar permeate concentration. (Martí-Calatayud et al., 2010). Oppositely TMP affected sugar permeation on membrane II, considerably incrementing sugar loss by 17-20 % at both high and low temperatures due to the smaller pore size with negligible improvement in colour removal and permeate fluxes. Since membrane I had the best performance in colour removal and sugar permeability, the highest TMP value of 8 bar and the highest temperature of 60 °C were beneficial to find a balance in the system by increasing permeate fluxes while avoiding membrane fouling.

4. Conclusions

Sustainable treatment of starch hydrolysates syrup by membrane technology has demonstrated the partial decolourization of the glucose syrup. UF membrane I with MWCO 70 kDa had the best performance removing around 27 % of the colour with a minimum sugar loss of 3 % at optimal operating conditions of 60 °C and 8 bar. Although colour separation in membrane I and membrane II is more efficient at 40 °C, the sugar permeability decreases considerably, indicating that 60 °C is more beneficial to increase the permeate fluxes in the system and the sugar permeability, but also having a considerable colour removal. Maximum permeate flux of 105 L/m2 with the minimum sugar loss and significant colour removal for membrane I is achieved when TMP was held at 8 bar. Nevertheless, process integration is recommended in this case to improve the membrane's performance and overcome the limited membrane selectivity in treating starch hydrolysates. Further study should consider a loose UF membrane (70 kDa) for initial and partial decolourization. Then its combination with another separation method should be evaluated to remove the remaining impurities in the final UF permeate. The new process could reduce energy costs and decrease chemicals and waste products in the current systems, as reported before in similar applications (Le Roux & Belyea, 1999). In addition, comparing the colour of the permeate and feed could give an estimation of the size of colour molecules of the starch hydrolysates. Thus, approximately 35 % of colour molecules are larger than 20-70 kDa, while the rest 70 % of molecules are smaller than 20 kDa.

Acknowledgments

The authors acknowledge financial support through the COMET Centre CHASE, funded within the COMET − Competence Centers for Excellent Technologies programme by the BMK, the BMDW and the Federal Provinces of Upper Austria and Vienna. The COMET programme is managed by the Austrian Research Promotion Agency (FFG). This project has also received the collaboration of Vienna University of Technology and AGRANA Research & Innovation Centre as an industrial partner.

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.

Alventosa-deLara E., Barredo-Damas S., Alcaina-Miranda M. I., Iborra-Clar M. I., 2012, Evolution of membrane performance during the ultrafiltration of reactive black 5 solutions: Effect of feed characteristics and operating pressure. Chemical Engineering Transaction*s*, *29*, 1285–1290.

Bhattacharya P. K., Agarwal S., De S., Gopal R., 2001, Ultrafiltration of sugar cane juice for recovery of sugar: analysis of flux and retention. *Separation and Purification Technology*, *21*(3), 247–259.

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 .

Cassano A., Drioli, E., 2014, Integrated membrane operations in the food production. Walter de Gruyter GmbH & Company, KG De Gruyter, Berlin, Germany.

Dziedzic S. Z., Kearsley M. W., 1995, Handbook of Starch Hydrolysis Products and Their Derivatives, Springer Science & Business Media.

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.

Gyura J., Šereš Z., Vatai G., Molnár E. B., 2002, Separation of non-sucrose compounds from the syrup of sugar-beet processing by ultra- and nanofiltration using polymer membranes. Desalination, 148(1-3), 49-56.

Hernández-Uribe J. P., Rodríguez-Ambriz S. L., Bello-Pérez L. A., 2008, Obtaining fructose syrup from banana starch (musa paradisíaca l.). Caracterización parcial. Interciencia, *33*(5), 372–376. (in Spanish)

Hobbs L., 2009, Sweeteners from starch: production, properties and uses. In *Starch* (pp. 797–832). Elsevier. Academic Press.

Le Roux L. D., Belyea R. L., 1999, Effects of ultrafiltration membrane concentration and drying temperature on nutritional value of biosolids from a milk processing plant. Bioresource Technology, 70(1), 17-21.

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.

Martí-Calatayud M. C., Vincent-Vela M.-C., Álvarez-Blanco S., Lora-García J., Bergantiños-Rodríguez E., 2010, Analysis and optimization of the influence of operating conditions in the ultrafiltration of macromolecules using a response surface methodological approach. Chemical Engineering Journal, *156*(2), 337–346.

Qi B, Wu Y., Guo S., Luo J., Wan, Y., 2017, Refinement of cane molasses with membrane technology for clarification and color removal. Journal of Membrane Science and Research, 3(4), 303-307.

Shahidi Noghabi M., Razavi S. M., 2015, Increase the Quality of Sugar by Ultrafiltration Process. Journal of Food Processing and Preservation, 39(6), 1192-1200.

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.

Singh N., Cheryan M., 1998, Properties and composition of concentrates and syrup obtained by microfiltration of saccharified corn starch hydrolysate. Journal of Cereal Science, *27*(3), 315–320.

Wang H. Y., Qian H., Yao W.R., 2011, Melanoidins produced by the Maillard reaction: Structure and biological activity. Food Chemistry, 128(3), 573-584.