Research Paper

Semi-pilot Tests of Ethanol Dehydration using Commercial Ceramic Pervaporation Membranes

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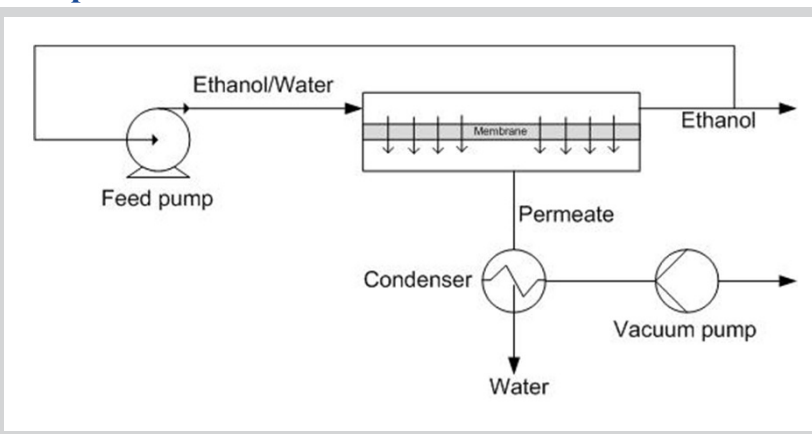## Article info

Keywords

Highlights

- Commercial hybrid silica membranes evaluation
- Ethanol dehydration process assessment from a process rather than from material's based perspective
- Benchmark semi-pilot results provided for attracting industrial interest

Graphical abstract

Abstract

Most research efforts about pervaporation in the literature have focused on membrane synthesis, trying to improve the membrane properties (flux and selectivity). However, industrial applications of the pervaporation technology could become attractive if the current available membranes proved to have sufficient and stable performance in order to be integrated in the toolbox of process engineers, as a complementary separation process. In this study, the ethanol dehydration performance of commercial hybrid silica membranes (HybSi®) was assessed in a semi-pilot pervaporation unit from a process-based perspective. The aim of the study is to reveal the high potential of the process and to create a benchmark for future studies in the field. The experimental results revealed that the proposed pervaporation process can efficiently break the ethanol/water azeotrope, allowing the production of high purity ethanol. The overall assessment of the obtained pilot results showed that the proposed process is quite efficient for attracting the industrial interest.

1. Introduction

Pervaporation (PV) is a potential alternative to state-of-the-art energy-intensive separation processes such as distillation. The separation mechanism in PV allows the separation of certain mixtures which cannot be separated by conventional distillation. More specifically, the feed in a PV process is a liquid mixture and only part of it is vaporized through a selective membrane to the permeate, which is held under vacuum. The permeate stream is enriched in the selectively permeating component, while, the retentate stream is enriched in the less permeable component and can be either collected or recycled for further processing (Figure 1). Typically, lower temperatures are required in PV than in conventional distillation. Generally, PV could find applications in separating azeotropic or close-boiling mixtures and volatile organic compounds, as well as in removing trace concentration components. Moreover, PV processes operate continuously (except the periodical membrane cleaning needed in some applications), having a completely modular design that allows an easy and flexible scale-up. All these perfectly fit to the current trends in process design and render PV technology very attractive, either as standalone or as hybrid separation process [1-3].
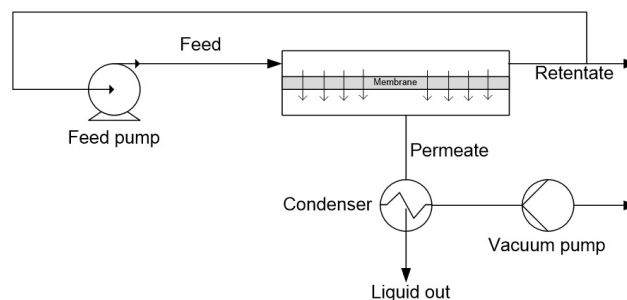

Fig. 1. Conceptual scheme of a typical pervaporation process.

Various types of polymeric, inorganic, and mixed matrix membranes have been studied in the literature mainly for the dehydration of solvents and especially alcohols forming azeotropes with water, like ethanol and isopropanol. Taking into account the continuously increasing interest in liquid biofuels produced from renewable biomass resources, as a means to reduce dependence on crude oil, it is evident why most of the research effort has been focused in this subject. In the production of bio-ethanol processes, pervaporation can be applied for product dehydration in order to meet fuel dryness specifications. Ethanol and water form an azeotrope at approximately 4.5 % w/w H_2O concentration. Conventionally this azeotrope can be broken via azeotropic distillation with the addition of another chemical component (e.g. cyclohexane) in the mixture. However this is an energy intensive process and the addition of another component to the initial mixture, poses additional impurities to be removed. Therefore, pervaporation can be considered as an alternative method of bio-ethanol dehydration which can break the azeotrope without the need for additional chemicals [4, 5].

Most pervaporation membranes that have been commercialized, mainly for small scale applications, are of polymeric, they are cheap and can be easily fabricated in large area membrane modules. Extensive research effort has been put in finding membrane materials with optimized separation properties towards the targeted mixture. However, these membranes are usually sensitive and their long-term performance is typically affected by process conditions and concentration of the main components and/or trace impurities. In this respect inorganic materials have some distinct advantages compared to polymeric ones, in terms of thermal and chemical stability. Ceramic membranes, a typical representative of this category, are resistant to temperatures and solvents that polymeric membrane could not withstand. They have also better mechanical stability, achieving thus a longer lifetime. Furthermore, ceramic membranes are typically more permeable than polymeric ones, reducing this way the membrane area needed for a specific application. Finally, the ceramic membranes are stable to several post-processing cleaning or regeneration techniques like back-flushing, steam sterilization or autoclaving. The recent advancements in ceramic membranes technology, allowed the synthesis and commercialization of ceramic membranes with well controlled pore size distributions and high selectivity which in turn led to increased interest in utilizing this type of membranes in pervaporation processes [6-8].

Hybrid (organic-inorganic) and mixed matrix (polymeric with inorganic fillers) membranes are composite materials which combine the characteristics of both phases or materials and provide improved properties that cannot be obtained from pure organic or inorganic membranes. Synthesis and characterization of both membrane types is an emerging research field with very high potential for many applications, including pervaporation [9, 10]. In the field of hybrid membranes, one of the most successful attempts up to date (which led to commercial membrane products), has been the synthesis of organo-silica materials, which have silicon atoms covalently bounded with organic groups. The introduction of organic groups (e.g. methyl-) into the silica matrix which leads to a significant improvement in the hydrothermal stability of silica membranes, is a representative example [11, 12].

Most research efforts about pervaporation in the literature have focused on new membrane materials and improved synthesis methods. Several different membranes have been developed, trying to improve the membrane separation properties (flux and selectivity). However, these membranes are often tested only in lab scale and remain very far from practical applications, mainly due to stability issues or complex and expensive fabrication methods. System design and process evaluation on the other hand, draw less attention. It has been pointed out that industrial penetration of pervaporation technology can be promoted by demonstrating the efficiency and stability of the current available membrane materials and not by trying to discover new and improved ones [13, 14]. Thus, the main target of this study is to assess the ethanol dehydration performance of commercial hybrid silica membranes (HybSi®) in a semi-pilot pervaporation unit, in order to create a benchmark for further studies in the field as well as for attracting the industrial interest.

2. Materials and methods

Tubular hybrid silica membranes (10 mm external diameter, 7mm internal diameter, 25 cm length, 0.005 m^2 effective membrane area) were procured from Pervatech BV and evaluated in this study. The membranes have an assymetric structure based on a tubular macroporous support and consecutive mesoporous and microporous inner layers. The final layer is typically the one which determines the separation efficiency of the membranes. The Pervatech hybrid silica membranes have hydrophilic character, meaning that H_2O passes preferentially through the membrane.

A semi-pilot pervaporation unit was designed and constructed in order to assess the performance of the membranes and the process. The unit can be operated either in a recycle or in a once-through mode. Special attention has been paid on designing a flexible unit capable to be used with different membranes and for various separation processes. The experimental unit consists of: (i) The Feed-Retentate section, consisting of a feed tank and an ISMATEK BVP-Z gear pump capable to deliver liquids in the membrane at elevated temperatures and pressures, (ii) The Membrane module section, consisting of a ceramic membrane tube, glaze sealed at two ends and compact sealed in a stainless steel housing with viton O-rings, (iii) the Permeate section, consisting of two parallel connected cold traps placed in vessels containing dry ice or liquid nitrogen for cooling and vapour condensation, and a Varian SD-91, dual stage rotary vane vacuum pump connected with an electronic Pirani Vacuum Gauge for absolute pressure measurement, (iv) the necessary tubing, valves and fittings (procured from Swagelok®) and instrumentation for process monitoring and safety issues. Figure 2 shows a detailed Process & Instrumentation Diagram (P&ID) of the experimental unit. It must be noted that all the parts of the Feed-Retentate and the Membrane module sections are insulated and can be heated up to 150 ºC, for high temperature operation.
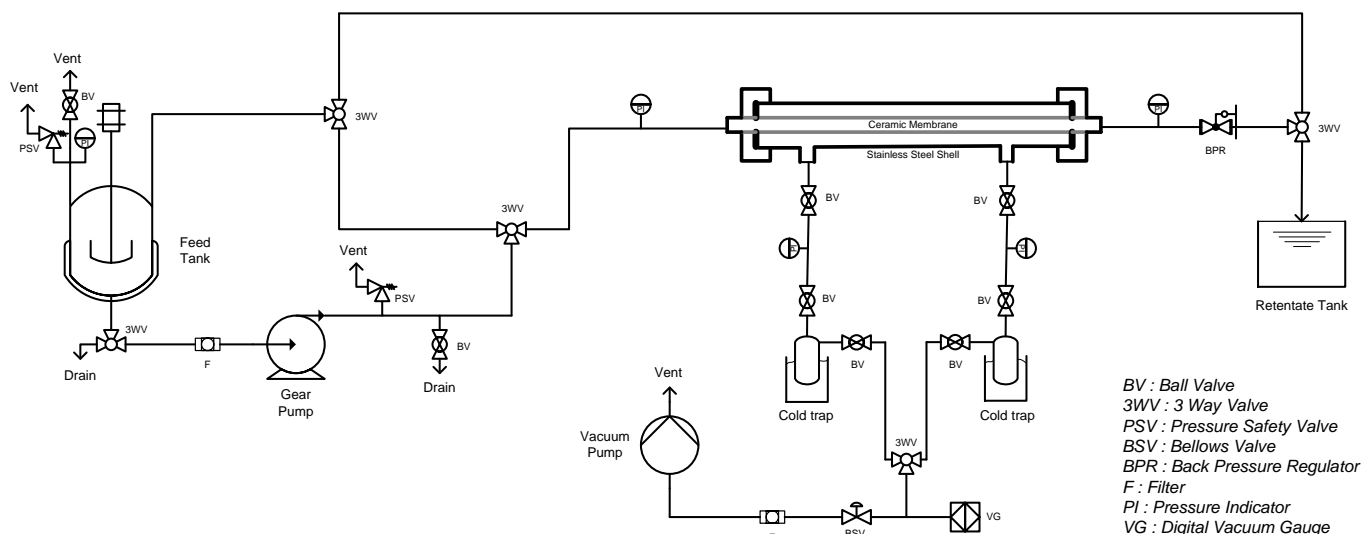

Fig. 2. P&ID of the custom-made pervaporation unit.

Typical ethanol pervaporation process conditions were selected for performance evaluation of HybSi® membranes. Specifically, the pervaporation tests were conducted at 75 °C and 1 bar of feed temperature and pressure respectively. Permeate pressure was maintained around 0.3-0.4 mbar and the permeate vapour was condensed using dry ice as coolant in the cold traps. Feed flow rate was regulated at 500 cc/min and the unit was operated in the recycle mode. 950 g of feed solution, consisting of 91.5% w/w EtOH and 8.5% w/w H_2O (selected to allow studying the pervaporation process around the azeotrope; EtOH/H_2O: 95.5/4.5 % w/w), was loaded in the Feed tank and the pervaporation process was studied with time by taking samples for analysis from the feed tank and the cold traps every 4 h. The quantitative analysis of feed and permeate samples was conducted using elemental analysis, using a LECO-800 CHN analyzer. Then the % mass concentration of C and H given by the elemental analysis method, were used to calculate the % composition of EtOH and H_2O in the samples. The applicability of the analysis method was confirmed by determining H_2O content in selected samples, using the Karl-Fischer titration method (ASTM E203-8).

3. Results and discussion

There is an ongoing debate in the literatures on which are the best indicators for reporting pervaporation performance data. Actually, there are two different approaches on that. The first is to report membrane performance data as intrinsic, driving force normalized properties like permeability, permeance and ideal selectivity. This helps to assess the performance of different membrane materials, since allows a straightforward comparison of membrane properties. The other way is to report the permeate flux and the separation factor which are more process oriented [15, 16]. In this case one must have in mind that when the pervaporation process is operated at the recycle mode (the most probable scenario) the system has a dynamic behavior and these properties vary with time. Despite that, operation parameters are more representative of a real case application, since the material parameters can be many times unrealistically high.

In this study the ethanol dehydration process assessment is based on concentration, recovery and purity data. The obtained experimental data are used to calculate the permeate flux (Eq. 1) and the separation factor (Eq. 2) as the most relevant process performance indicators. These parameters are different from permeance and permselectivity measurements which represent ideal membrane properties. Specifically, the separation factor is representative of the process' real separation performance and not just the ratio of two components permeance.

$$J_t = \frac{m_t^P}{A \times \Delta t} \tag{1}$$

$$\beta_t = \frac{\left(\dfrac{c_{H2O}^P}{c_{EtOH}^P}\right)_t}{\left(\dfrac{c_{H2O}^F}{c_{EtOH}^F}\right)_0} \tag{2}$$

Figure 3 shows the H_2O content in the feed tank and in the accumulated permeate stream with time. The graph shows an almost linear decrease in H_2O feed tank content with time. This is due to the selective permeation of H_2O through the membrane from feed to permeate side. Specifically, after 32 h of feed treating in the pervaporation unit the H_2O concentration reduces from 8.5% to less than 0.5% w/w. This is a significant achievement since the EtOH/H_2O mixture forms an azeotrope at 95.5/4.5% w/w composition, with a boiling point of 78.2 °C, which means that the reduction of H_2O content of the mixture at values lower than 4.5% w/w cannot be performed by simple distillation. Thus, it is evident that, this barrier can be overcome by the proposed pervaporation method. The same trend is also observed in the accumulated permeate stream, where the H_2O content reduces from 84% (at 4h of operation) to 77% (at 32 h of operation). This is caused by the gradual decrease of H_2O concentration (and the implied increase of EtOH concentration) in the feed side which reduces the ratio of H_2O to EtOH permeation rate with time.

The ultimate target of the specific pervaporation application was to purify ethanol by removing H_2O. However, as in every membrane process, there is a trade-off between final product's purity (% wt EtOH in the feed tank) and its recovery (% EtOH in the feed tank with respect to the initial). Figure 4 shows this trade-off for the specific application. The first in chronological order point in the graph (upper left) represents the initial concentration of the feed solution and every next point corresponds to 4h time steps of unit operation.

The same behavior (recover-purity tradeoff) can also be observed in the permeate side with H_2O recovery (% H_2O in the permeate stream with respect to the initial in the feed tank) and purity (% wt H_2O in the permeate stream), as shown in Figure 5. The first in chronological order point in the graph (bottom right) represents H_2O recovery and purity after 4h of unit operation and every next point corresponds to extra 4h of operation. It must be noted that in the permeate side, H_2O recovery-purity curve has the opposite trend with time, since as more H_2O moves from Feed to Permeate side, H_2O recovery increases and its purity decreases.

Figures 6 and 7 show permeate flux and separation factor with time for the pervaporation process as calculated from Eqs. 1-2. The first points in the graphs represent parameter values calculated by weighting and analyzing permeate collected in the 0-4h time period, while next points represent the accumulative results for the 0-8h, 0-12h, etc. time periods. Both of these parameters can be considered as process parameters, rather than membrane properties.

The initial permeate flux at the tested process conditions was calculated to be 1.03 kg·m^{-2}·h^{-1} and gradually reduced with time, as the driving force is reduced. The calculated value is comparable to others reported in the literature for similar types of membrane materials and process conditions. Moussa et al. [8] used methylated silica membranes and measured a water flux about 0.6 kg·m^{-2}·h^{-1} for an EtOH/H_2O: 94/6 w/w binary mixture at at 60 °C. Similarly, van Veen et al. [17] tested silica membrane for dewatering of several organic solvent and they reported a water flux about about 1.22 kg·m^{-2}·h^{-1} for an EtOH/H_2O: 94.5/5.5 w/w binary mixture at 70 °C. Finally, Urtiaga et al. [18], tested two different commercial silica membranes for dehydration of ketonic effluents and they reported water fluxes about 0.52 and 2.7 kg·m^{-2}·h^{-1} respectively, for a feed mixture with 10% w/w H_2O content at at 70 °C.
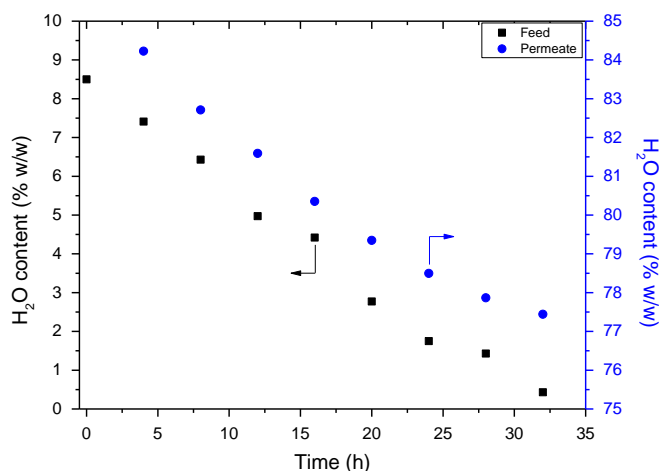

Fig. 3. H_2O content in the feed tank and accumulated permeate stream with pervaporation operation time.
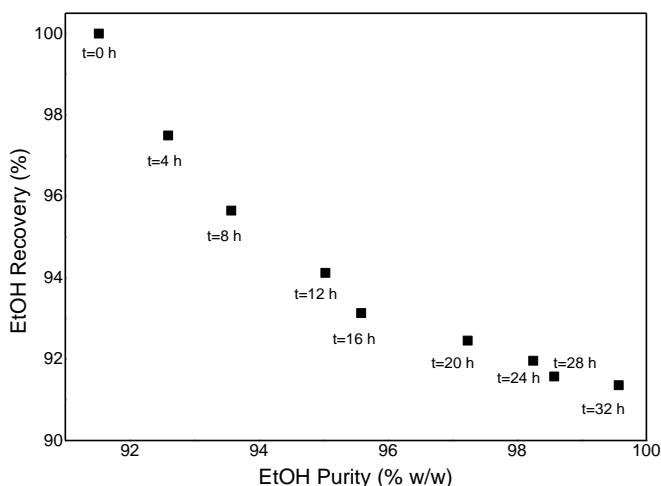

Fig. 4. EtOH recovery-purity trade-off for the pervaporation process.

The separation factor, which is indicative of the separation achieved with the applied process, is quite high and demonstrates the high potential of the pervaporation process with HybSi® membranes. It is evident that both permeate flux as well as separation factor reduce with time because H_2O concentration in the feed side and subsequently the process driving force is also reduced.

The scale-up potential of the process was assessed as an additional attempt to promote the industrial penetration of the technology. A production rate of 1000 kg/h of fuel grade ethanol (>99.5% w/w) was set as the basis for the calculations. Figure 8 shows the estimated membrane area needed for the production of 1000 kg/h ethanol (99.57% w/w) with the initial H_2O content in the feed. Estimations were based on the experimental measurements (feed and permeate analysis and weighting) and the process mass balance calculations.

Results show that the membrane area needed for the production of fuel grade ethanol increase with the initial H_2O content of the feed, as expected, since more H_2O has to be removed. Membrane areas in the range of about 25-200 m^2 were calculated for feed H_2O content in the range 1.4-8.5% w/w. A linear regression analysis was added in the graph trying to estimate the correlation between them. In the worst case scenario about 200 m^2 of membrane area are needed for the production of 1000 kg/h of fuel grade ethanol from 1190kg/h of feed with 8.5% w/w H_2O. Currently, Pervatech BV offers modules with available membrane area up to 3.8 m^2, based on information retrieved from its website [19]. This means that about 53 membrane modules would needed to achieve the target, although the potential manufacturing of larger area membrane modules could be probably considered for an industrial application of this scale. Trying to estimate the main operating expenses of the process, a preliminary energy analysis of the process was conducted, using Aspen Plus. The results indicated that vacuum generation is the most energy intensive part of the process, with about 66.5 kW to be needed for the worst case scenario (190.5 kg/h of permeate removed at 0.3 mbar). The respective energy consumption of the feed pump is more than an order of magnitude lower, about 1.35 kW. Although the energy needed to heat the feed process stream from 20 to 75 °C is about 59.7 kW, it must be noted that the relative low operating temperature allows the exploitation of waste heat from other process streams for this purpose. These results could serve as the basis for detailed technoeconomic assessment of the process. In this regard, previous technoeconomic studies have shown that a hybrid distillation-pervaporation schemes are superior in terms of energy efficiency and more environmental friendly than the conventional azeotropic distillation schemes [20, 21].

4. Conclusions

The ethanol dehydration process using commercial hybrid silica pervaporation membranes (HybSi®) was studied in a semi-pilot pervaporation unit from a process-based perspective. Experimental results revealed that the azeotrope formed at 95.5/4.5% w/w EtOH/H_2O can be overcome and H_2O concentration can be reduced to less than 0.5% w/w, recovering more than 91% of initial EtOH, by employing the proposed pervaporation process. The obtained fluxes and separation factors are sufficiently high and comparable to similar studies in the literature. It is therefore evident that the proposed process and membrane material are suitable for attracting industrial interest.
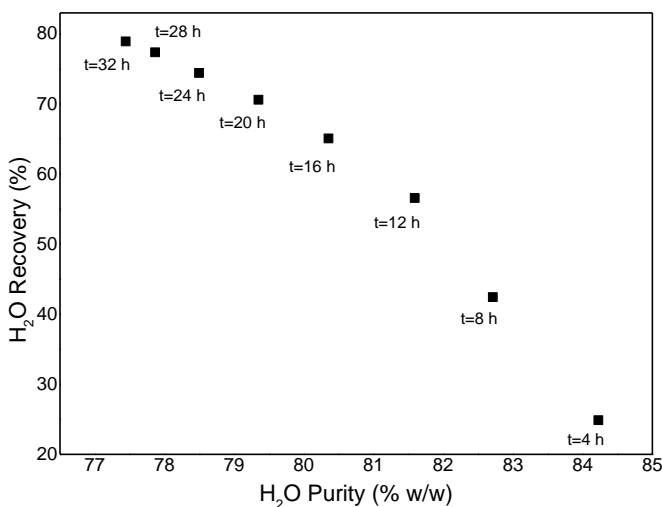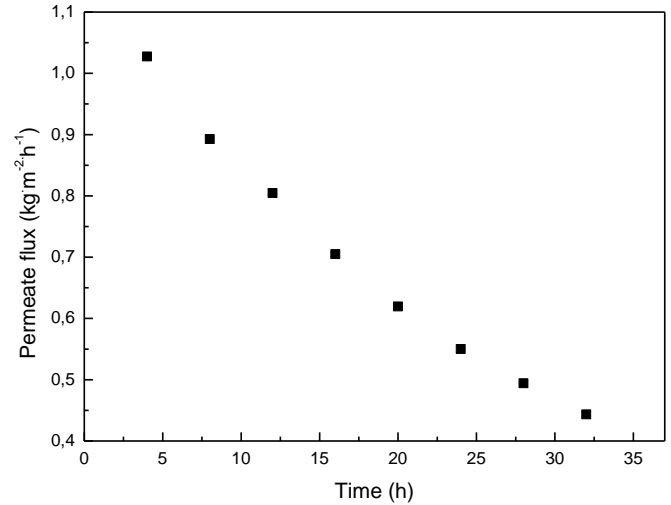

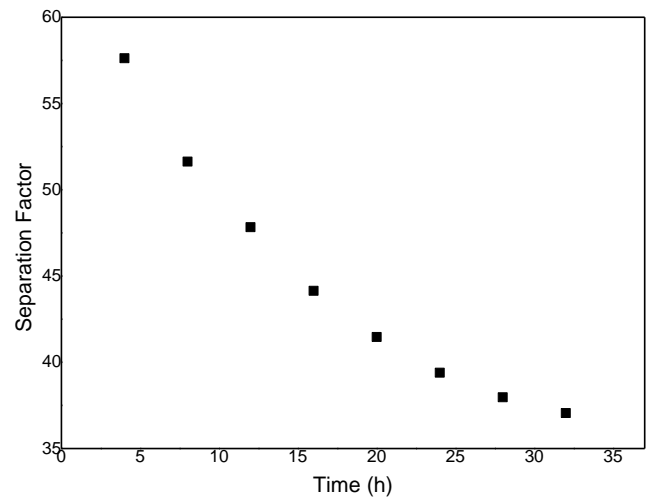**Fig. 6.** Permeate flux with time in the pervaporation process.

Fig. 7. Separation factor with time in the pervaporation process.

Nomenclature

J_t : permeate flux, $kg/(m^2 \cdot h)$
m: permeate mass, kg
A: membrane area, m^2
Δt: time interval, h
β: separation factor, $[-]$
c: mass concentration (w/w), $[-]$

Subscripts

t: at time point t
0: at time point 0 (initial)

Superscripts

P: permeate
F: Feed

Fig. 5. H_2O recovery-purity trade-off for the pervaporation process.

Linear fit

T = 75 °C

Membrane area (m^2)

H$_2$O content in the feed (% w/w)

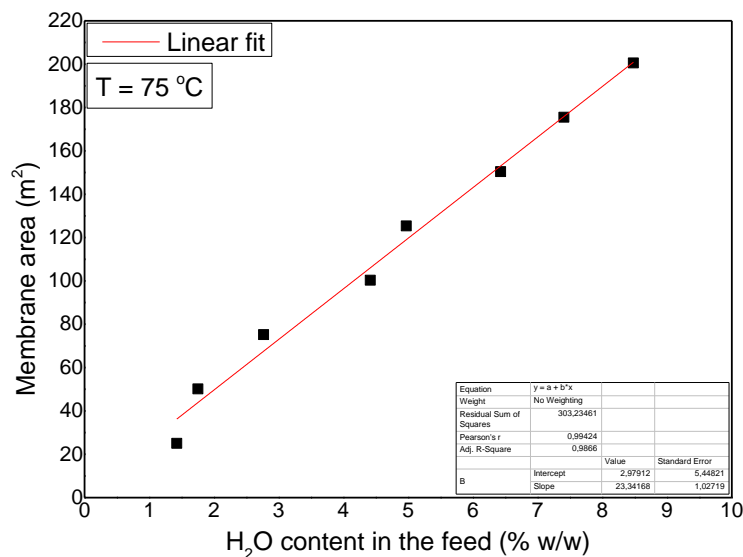| Equation	y = a + b*x	
Weight	No Weighting	
Residual Sum of Squares	303,23461	
Pearson's r	0,99424	
Adj. R-Square	0,9866	
	Value	Standard Error
B Intercept	2,97912	5,44821
Slope	23,34168	1,02719

Fig. 8. Membrane area needed for the production of 1000 kg/h fuel grade ethanol with the H$_2$O content in the feed.

References

[1] S. Zhang, E. Drioli, Pervaporation Membranes, Separ. Sci. Tech. 30 (1995) 1-31. https://doi.org/10.1080/01496399508012211

[2] T.S. Bowen, R.D. Noble, J.L. Falconer, Fundamentals and applications of pervaporation through zeolite membranes, J. Membr. Sci. 245 (2004) 1-33. https://doi.org/10.1016/j.memsci.2004.06.059

[3] J. Wang, T. Tsuru, Cobalt-doped silica membranes for pervaporation dehydration of ethanol/water solutions, J. Membr. Sci. 369 (2011) 13-19. https://doi.org/10.1016/j.memsci.2010.10.062

[4] M.A. Sosa, D.A.F. Paredes, J.C. Basilico, B. Van der Bruggen, J. Espinosa, Screening of pervaporation membranes with the aid of conceptual models: An application to bioethanol production, Separ. Purif. Tech. 146 (2015) 326-341. https://doi.org/10.1016/j.seppur.2015.04.001

[5] P.D. Chapman, T. Oliveira, A.G. Livingston, K. Li, Membranes for the dehydration of solvents by pervaporation, J. Membr. Sci. 318 (2008) 5-37. https://doi.org/10.1016/j.memsci.2008.02.061

[6] A.W. Verkerk, P. van Male, M.A.G. Vorstman, J.T.F. Keurentjes, Description of dehydration performance of amorphous silica pervaporation membranes, J. Membr. Sci. 193 (2001) 227-238. https://doi.org/10.1016/S0376-7388(01)00516-6

[7] S.-L. Wee, C.-T. Tye, S. Bhatia, Membrane separation process – Pervaporation through zeolite membrane, Separ. Purif. Tech. 63 (2008) 500-516. https://doi.org/10.1016/j.seppur.2008.07.010

[8] M. Moussa, I. Souchon, V. Athès, Pervaporative Dehydration of Binary Ethanol/Water and Ternary Ethanol/Water/Methanol Mixtures Using a Methylated Silica Membrane: A Mechanistic Approach, Separ. Sci. Tech., 50 (2015) 2708-2716. https://doi.org/10.1080/01496395.2015.1071849

[9] Z. Xie, M. Hoang, T. Duong, D. Ng, B. Dao, S. Gray, Sol–gel derived poly(vinyl alcohol)/maleic acid/silica hybrid membrane for desalination by pervaporation, J. Membr. Sci. 383 (2011) 96-103. https://doi.org/10.1016/j.memsci.2011.08.036

[10] V.C. Souza, M.G.N. Quardi, Organic-inorganic hybrid membranes in separation processes: a 10 year review, Brazil. J. Chem. Eng. 30 (2013) 683-700. https://doi.org/10.1590/S0104-66322013000400001

[11] H.L. Castricum, R. Kreiter, H.M. van Veen, D.H.A. Blank, J.F. Vente, J.E. ten Elshof, High-performance hybrid pervaporation membranes with superior hydrothermal and acid stability, J. Membr. Sci. 324 (2008) 111-118. https://doi.org/10.1016/j.memsci.2008.07.014

[12] I. Agirre, P.L. Arias, H.L. Castricum, M. Creatore, J.E. ten Elshof, G.G. Paradis, P.H.T. Ngamou, H.M. van Veen, J.F. Vente, Hybrid organosilica membranes and processes: status and outlook, Separ. Purif. Tech. 121 (2014) 2-12. https://doi.org/10.1016/j.seppur.2013.08.003

[13] B. Van der Bruggen, P. Luis, Pervaporation as tool in chemical engineering: a new era?, Cur. Opin. Chem. Eng. 4 (2014) 47-53. https://doi.org/10.1016/j.coche.2014.01.005

[14] A. Khalid, M. Aslam, M.A. Qyyum, A. Faisal, A.L. Khan, F. Ahmed, M. Lee, J. Kim, N. Jang, I.S. Chang, A.A. Bazmi, M. Yasin, Membrane separation processes for dehydration of bioethanol from fermentation broths: Recent developments, challenges, and prospects, Renew. Sustain. Ener. Rev. 105 (2019) 427-443. https://doi.org/10.1016/j.rser.2019.02.002

[15] J.G. Wijmans, Letter to the Editor, J. Membr. Sci, 220 (2003) 1-3. https://doi.org/10.1016/j.memsci.2003.08.003

[16] R.W. Baker, J.G. Wijmans, Y. Huang, Permeability, permeance and selectivity: A preferred way of reporting pervaporation performance data, J. Membr. Sci. 348 (2010) 346-352. https://doi.org/10.1016/j.memsci.2009.11.022

[17] H.M. van Veen, Y.C. van Delft, C.W.R. Engelen, P.P.A.C. Pex, Dewatering of organics by pervaporation with silica membranes, Separ. Purif. Tech. 22-23 (2001) 361-366. https://doi.org/10.1016/S1383-5866(00)00119-2

[18] A.M. Urtiaga, E.D. Gorri, P. Gómez, C. Casado, R. Ibáñez, I. Ortiz, Pervaporation technology for the dehydration of solvents and raw materials in the process industry, Drying Tech. 25 (2007) 1819-1828. https://doi.org/10.1080/07373930701677975

[19] https://pervaporation-membranes.com/products/modules/, Retrieved January 12 2021

[20] D. Kunnakorn, T. Rirksomboon, K. Siemanond, P. Aungkavattana, N. Kuanchertchoo, P. Chuntanalerg, K. Hemra, S. Kulprathipanja, R.B. James, S. Wongkasemjit, Techno-economic comparison of energy usage between azeotropic distillation and hybrid system for wateree thanol separation, Renew. Ener. 51 (2013) 310-316. https://doi.org/10.1016/j.renene.2012.09.055

[21] P. Fasahati, J.J. Liu, Economic, energy and environmental impacts of alcohol dehydration technology on biofuel production from brown algae, Energy 93 (2015) 2321-2336. https://doi.org/10.1016/j.energy.2015.10.123