Systems & Control Transactions

Research Article - Peer Reviewed Conference Proceeding
ESCAPE 35 - European Symposium on Computer Aided Process Engineering
Ghent, Belgium. 6-9 July 2025
Jan F.M. Van Impe, Grégoire Léonard, Satyajeet S. Bhonsale,
Monika E. Polańska, Filip Logist (Eds.)

PSE PRESS

Synthesis of Liquid Mixture Separation Networks Using Multi-Material Membranes

Harshit Verma[a], Christos T. Maravelias[a,b,*]

[a] Princeton University, Department of Chemical and Biological Engineering, Princeton, New Jersey, USA
[b] Andlinger Center for the Energy and Environment, Princeton University, Princeton, New Jersey, USA
* Corresponding Author: maravelias@princeton.edu.

ABSTRACT

The synthesis of membrane networks to recover components from liquid mixture is challenging due to an extensive array of feasible network configurations and the added complexity of modeling membrane permeators caused by nonidealities in liquid mixtures. We present a mixed-integer nonlinear programming (MINLP) framework for synthesizing membrane networks to recover multiple components from liquid mixtures. First, we develop a physics-based nonlinear surrogate model to accurately describe crossflow membrane permeation. Second, we propose a richly connected superstructure to represent numerous potential network configurations. Third, the two aforementioned elements are integrated into an MINLP model to determine the optimal network configuration. Finally, the effectiveness of the proposed approach is demonstrated through a range of applications.

Keywords: Liquid Mixture Separations, Membrane Network Synthesis, Superstructure-based Optimization, Mixed-Integer Nonlinear Programming.

INTRODUCTION

Membranes for liquid separation are recognized as a promising technology, offering several advantages including low energy requirements and chemical-free operation [1]. Polymeric membranes, in particular, have emerged as a preferred choice due to their scalability. The two key properties of polymeric membranes are permeability and selectivity. High permeability facilitates enhanced recovery, while high selectivity ensures high purity. However, polymeric membranes inherently exhibit a trade-off between selectivity and permeability [2]. Therefore, utilizing a single-stage membrane unit to achieve both high recovery and purity simultaneously is often impractical or incurs high operating and capital costs. To address this limitation, a multi-stage membrane network must be synthesized.

Multiple configurations of membrane networks, differentiated by the number of membrane stages and stream connections, can be synthesized for a given separation task. However, the energy consumptions and capital costs of these configurations can vary significantly depending on the total utilized membrane area and the operating conditions. The two primary methods for synthesizing membrane networks are simulation-based and optimization-based methods. In the former, a network is chosen from various potential network configurations and the operating conditions are subsequently determined [3]. However, with an increase in the number of membrane stages, this method becomes increasingly cumbersome due to the significant increase in the number of potential network configurations, so only a limited number of network configurations can be evaluated, potentially leading to suboptimal designs. In optimization-based methods, the network configuration and operating conditions are determined simultaneously by solving an optimization model [4]. In general, a superstructure is constructed to include all potential network configurations. Then, a mixed-integer nonlinear programming (MINLP) model is formulated based on the superstructure, with binary and continuous variables used to represent the configurational and operational decisions, respectively. However, the accuracy of unit models is limited due to the approximations required to formulate a computationally tractable optimization model. This work

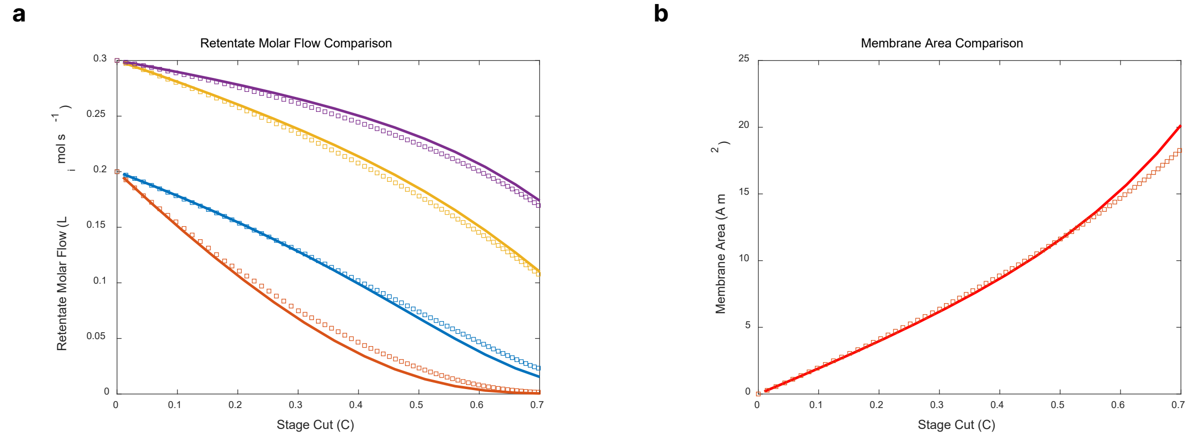

Figure 1: Comparison between the NLAE (solid lines) and the DAE (square markers) unit model. **a,** Retentate flow rate comparison: Blue, orange, yellow, and violet colors represent the flow rate of methyl acetate, ethyl acetate, isopropanol, and 1-butanol, respectively. **b**, membrane area comparison.

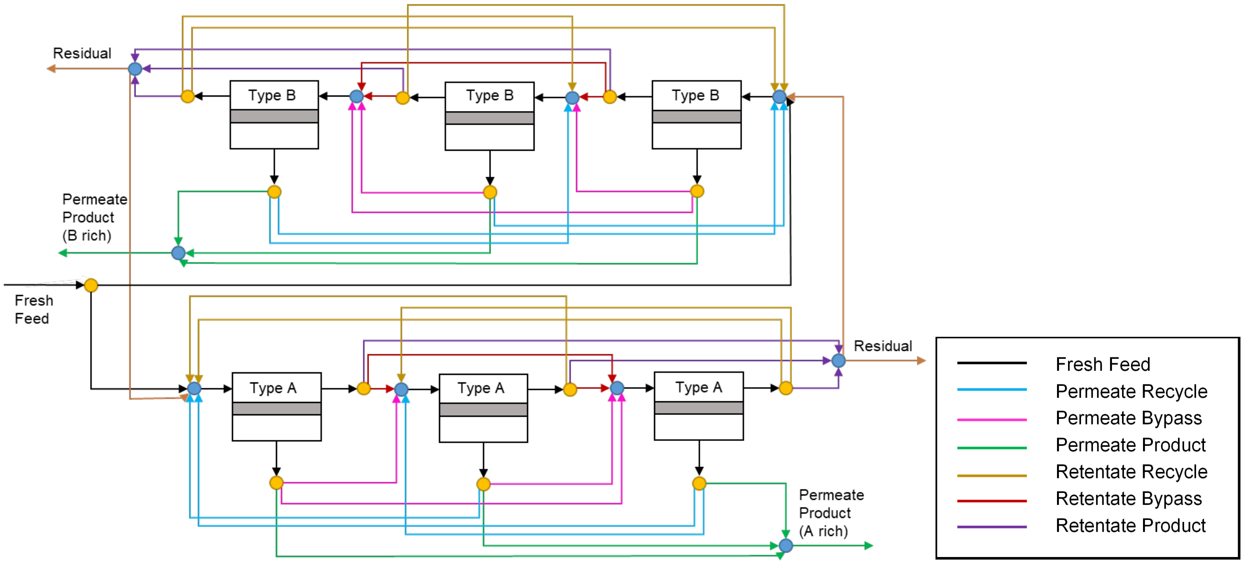

Figure 2: Schematic of a superstructure with two sub-network, each with three stages, with distinct membrane types. Yellow and blue disks represent splitters and mixers, respectively.

addresses this limitation by using an accurate membrane unit model.

Various membrane unit models for gas separation have been proposed. Marriott and Sørensen incorporated mass, momentum, and energy balances, employing partial differential-algebraic equations (PDAE), to model membrane separation [5]. The crossflow models proposed by Weller and Steiner [6] and Shindo et al. [7], formulated as differential-algebraic equations (DAE), have been commonly utilized to model the separation of gas and liquid mixture. However, integrating PDAE/DAE systems in an optimization model to achieve a globally optimal solution presents significant challenges [8]. Thus, various discretization techniques are employed to reformulate the PDAE/DAE systems into a system of algebraic equations. However, discretization schemes involve a trade-off between model complexity and solution accuracy. While finer discretization provides high accuracy, it also increases the number of nonlinear equations, making it computationally challenging to attain global optimality. Additionally, building on the work of Weller and Steiner [6] and Shindo et al. [8], Chen et al. [9] and Taifan and Maravelias [10] developed a unit model for the separation of multicomponent gas mixtures. Moreover, Chavez Velasco et al. [11] developed a unit model specifically for the separation of binary liquid mixtures. As a result, current unit models are limited to the separation of either binary liquid mixtures or multicomponent gas mixtures. Thus, there is a critical gap in the development of membrane unit models for the separation of multicomponent liquid mixtures.

Numerous computational methods have been proposed for the synthesis of membrane networks. Pathare and Agrawal [12] devised a method that systematically enumerates all networks and solves a nonlinear program (NLP) for each. However, this approach becomes increasingly computationally intensive as the number of potential networks increases. Other existing optimization models for synthesizing membrane networks typically rely on local optimization or meta-heuristic methods [13–15]. The studies aiming to obtain global optimality generally focus on the separation of binary mixtures [11,14]. Moreover, the optimization models developed by Chen et al. [9] and Taifan and Maravelias [10] specifically target multicomponent gas mixtures and impose restrictions on the stream connections within the membrane network superstructure. This limitation excludes some feasible network configurations, potentially leading to suboptimal solutions.

In this work, we present a novel approach for synthesizing optimal membrane networks for multicomponent liquid mixture separation [16]. We propose a generalized optimization model that incorporates three elements. First, we develop a physics-based nonlinear surrogate unit model to describe crossflow membrane permeation for multicomponent liquid mixtures. Second, we propose a highly interconnected superstructure to represent an extensive array of potential network configurations. Third, we formulate an optimization model to determine the configuration and operating conditions that minimize the total required membrane area. Finally, we present multiple applications to showcase the effectiveness of our approach.

MEMBRANE UNIT MODEL

First, we adapt the DAE-based crossflow membrane unit model from Shindo et al. [7] for multicomponent liquid mixtures. Next, the DAE unit model is reformulated to a nonlinear algebraic unit model (NLAE). Finally, we assess accuracy by comparing the NLAE unit model with the original DAE model.

DAE Unit Model

In an idealized crossflow membrane unit, the liquid mixture on the feed-side exhibits plug flow with no longitudinal mixing. The permeating components selectively pass through the membrane and enter the permeate-side without mixing with the permeate bulk flow. The DAE unit model is based on the following assumptions: (1) component permeabilities are independent of pressure and composition, (2) material transport follows Fick's law of diffusion, (3) negligible concentration polarization, (4) only transmembrane pressure drop is observed, (5) isothermal operation, (6) negligible mass transfer resistance, and (7) uniform membrane thickness. In the DAE model, material transport across polymeric membranes is described by the solution-diffusion theory, which has been widely employed and extensively validated against experimental data from physical systems [17]. The DAE unit model for the pervaporation process is given by the following equations [7]:

$$\frac{dF_i^{\mathrm{F}}}{dA} = -\pi_i\left(G_i\hat{X}_i - \tau_i\hat{Y}_i\right) \qquad \forall\, i \in \mathbf{I} \tag{1}$$

$$\hat{Y}_i = \frac{\pi_i(G_i\hat{X}_i - \tau_i\hat{Y}_i)}{\sum_{i' \in \mathbf{I}} \pi_{i'}(G_{i'}\hat{X}_{i'} - \tau_{i'}\hat{Y}_{i'})} \qquad \forall\, i \in \mathbf{I} \tag{2}$$

$$\dot{F}^{\mathrm{F}}\hat{X}_i = F_i \qquad \forall\, i \in \mathbf{I} \tag{3}$$

$$F_i^{\mathrm{F}}\Big|_{\dot{F}^{\mathrm{F}} = \dot{F}} = F_i \qquad \forall\, i \in \mathbf{I} \tag{4}$$

where $\hat{X}_i/\hat{Y}_i$ represent the molar fraction of component i on the feed-side/permeate-side, while F_i^{F}/F_i and $\dot{F}^{\mathrm{F}}/\dot{F}$ denote the molar flow rate of component i in the feed-side/fresh feed and the total molar flow rate in the feed-side/fresh feed, respectively; $G_i, \tau_i,$ and π_i represent the activity coefficient, normalized permeate pressure, and permeance of component i, respectively. Finally, given the initial conditions and the desired separation specifications, composition profiles and the required membrane area can be determined.

NLAE Unit Model

Discretization schemes are primarily employed to convert DAE systems into algebraic equations. However, this approach increases computational complexity, making it difficult for optimization solvers to achieve global optimality. We utilize a different approach, based on the assumption of a uniform collective driving force, B, and activity coefficients, G_i, across the membrane surface. The DAE model can be reformulated into differential equations, which can be integrated to obtain the following set of nonlinear algebraic equations:

$$\ln\left(\frac{L_i}{F_i}\right) = \left(\frac{\pi_i G_i}{B + \pi_i\tau_i}\right)\ln(1 - C) \qquad \forall\, i \in \mathbf{I} \tag{5}$$

$$\sum_{i \in \mathbf{I}} L_i = (1 - C)\sum_{i \in \mathbf{I}} F_i \tag{6}$$

$$A = \frac{1}{B}\left(\dot{F} - \dot{L}\right) \tag{7}$$

where F_i/L_i and $\dot{F}/\dot{L}$ are the molar flow rates of component i and the total molar flow rate in the feed/retentate stream, while C and A represents the stage cut and the required area, respectively. Detailed reformulation steps are provided in the Supplementary Material. Further, the accuracy of the NLAE unit model is essential for its integration in the optimization model. Thus, we validate the developed NLAE unit model by comparing it with the DAE unit model using simulations in MATLAB, focusing on two key variables: the retentate flow rate and the membrane area, under varying final stage cut, C, for both models. Data for the simulation is provided in the Supplementary Material. For the DAE unit model, the retentate flow rate and the membrane area are determined by solving Eq. $(1), (2), (3),$ and (4), while

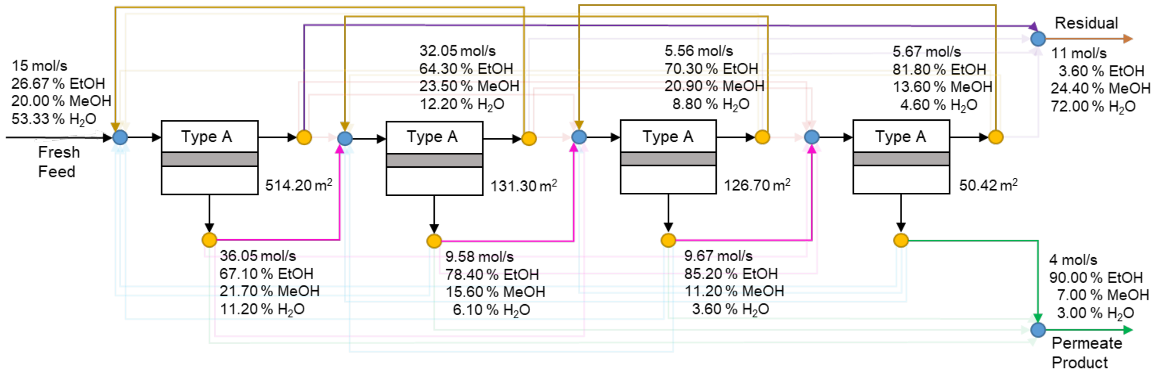

Figure 3: Single component separation: global optimal network to recover EtOH at the desired recovery and purity of 90%.

for the NLAE unit model, they are calculated using Eq. $(5), (6),$ and (7). Consequently, the comparison between the two unit models, shown in Figure 1, demonstrates good agreement.

SUPERSTRUCTURE REPRESENTATION

We present a superstructure with rich interconnections designed to recover multiple target components from a liquid mixture. The superstructure can employ distinct membrane materials, each specifically selective for different target components. Moreover, it incorporates multiple sub-networks that are interconnected to achieve the required separation task. Within each sub-network, the superstructure employs a unique membrane material and allows for: (1) a retentate/permeate to be sent to any of the previous stages as a retentate/permeate recycle, (2) a retentate/permeate to be sent to any of the subsequent stages as a retentate/permeate bypass, and (3) a retentate/permeate to be collected from any stage as a retentate/permeate product. The permeate final product from a sub-network contains a recovered target component, while the retentate final product is fed into other sub-networks for further separation of remaining target components. Additionally, each sub-network utilizes one mixer for each feed entering a stage, two mixers for retentate and permeate products, two splitters for each retentate and permeate leaving a stage, and one splitter for the fresh feed stream. Finally, to minimize the number of symmetrical solutions, the fresh feed is allowed to enter only the first stage of each sub-network. For illustration, Figure 2 shows a schematic of a superstructure with two sub-networks, each with three stages employing Type A and Type B membranes, to recover target components A and B from a liquid mixture, respectively.

In the mathematical formulation, binary variables are utilized to denote the activation of membrane stages for specific membrane types. Thus, the binary variable $Z_{n,m}$ is introduced to denote whether stage n of membrane type m is active. Additionally, the location of the fresh feed inlet to one of the sub-networks plays a critical role. Therefore, the binary variable Y_m is used to denote if the fresh feed enters the sub-network with membrane type m. Further, material balances are introduced around all the mixers, splitters, and around each stage of the sub-network. A detailed mathematical formulation is provided in the Supplementary Material. In practical applications, condensers and pumps are utilized to condense permeate vapors and adjust the pressure of the permeate stream for further recycling, bypassing, or collection of the permeate. However, the objective of the proposed model is to minimize the overall membrane area. Thus, calculations for condenser and vacuum pump units are excluded.

APPLICATIONS

First, we study the behaviour of a membrane network that utilizes a single sub-network with a unique material for the separation of one target component from an alcohol/water mixture. Second, we show the effectiveness of the proposed method using an example with three components for the simultaneous separation of two target components. All optimization models are written in GAMS 46.4.1 and are solved using BARON 24.3.10 on a Windows machine with a 1.60 GHz CPU and 32 GB RAM.

Single Component Separation

We analyze a membrane network system that processes a fresh feed, pressurized at 1 atm with a flow rate of 15 mol/s, of an alcohol/water mixture. The mixture consists of 26.67% ethanol (EtOH), 20% methanol (MeOH) and 53.33% water (H_2O) on a molar basis. The feed-side pressure in a membrane unit is set to match the pressure of the fresh feed, while the permeate-side pressure is maintained at 0.01 atm to facilitate pervaporation. Isothermal operation is assumed at 323.15 K. The permeance values for EtOH, MeOH, and H_2O for an ethanol-selective membrane are 0.088, 0.051, 0.018 (mol/m^2/s), and for a methanol-selective membrane type are 0.025, 0.18, 0.018 (mol/m^2/s) respectively, which fall in the range of Nafion membranes.

The proposed model is employed with a single membrane type, thus we construct a four-stage superstructure with an ethanol-selective membrane type (Type A), as shown in Figure S1. First, we determine the optimal network for the separation of ethanol from the liquid mixture at the desired purity and recovery of 90%. The model contains 309 equations and 247 variables (4 binaries) and is solved to global optimality within 60 s. The global optimal network configuration, shown in Figure 3, requires four membrane stages with a total area of 204.87 m^2. In the optimal network, EtOH permeates through the active stages of Type A membrane and is bypassed to the subsequent stages, facilitating effective separation by concentrating the EtOH rich permeate. Accordingly, the final permeate product is collected from the last stage meeting the higher recovery and purity specifications, while the residual mixture is collected as the retentate final product.

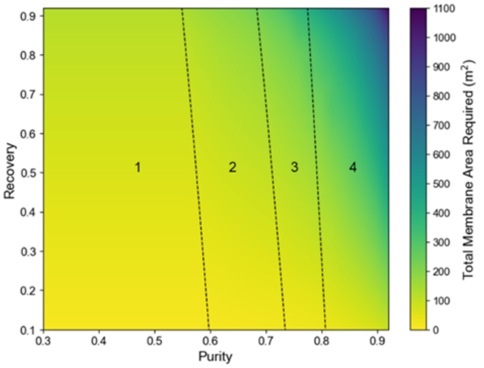

Figure 4: Total membrane area and number of required stages under varying recovery and purity specifications.

Next, we study the impact of purity and recovery specifications for EtOH on the network's configuration and operation by solving the model under varying purity and recovery specifications. Figure 4 illustrates the variation in the total required area and the number of stages needed as the desired recovery and purity increase. Accordingly, the purity specification significantly influences the network design, including the number of required stages and the total required area, compared to the specified recovery. However, the purity threshold for installing an additional stage is lower at higher recovery, suggesting a modest impact of specified recovery on network performance.

Two Component Separation

The separation and recovery of iso-butanol (i-BuOH) and ethanol (EtOH) are of significant importance in biological systems, particularly in the context of biofuel production and sustainable energy solutions. However, their separation presents challenges due to their similar boiling points and azeotropic behaviours. Therefore, membrane-based separation technology can be employed to effectively recover both i-BuOH and EtOH. In this example, we study the simultaneous separation and recovery of i-BuOH and EtOH from an aqueous mixture using a multi-material membrane network system. We consider a fresh feed pressurized at 1 atm with a flow rate of 15 mol/s, consisting of an aqueous i-BuOH/EtOH mixture. This mixture comprises 26.67% i-BuOH, 20% EtOH and 53.33% water (H_2O) on a molar basis. The feed-side pressure in a membrane unit is set to match the pressure of the fresh feed, while the permeate-side pressure is maintained at 0.01 atm to facilitate pervaporation. Isothermal operation at 323.15 K is assumed. Permeance values for i-BuOH, EtOH, and H_2O for an iso-butanol-selective membrane are 0.057, 0.023, 0.017 (mol/m^2/s), and for an ethanol-selective membrane type are 0.004, 0.138, 0.017 (mol/m^2/s), respectively.

We employ an iso-butanol-selective membrane type (Type A) and an ethanol-selective membrane type (Type B) across two interconnected sub-networks (see Figure 2). Additionally, we allow each sub-network to include four stages to facilitate separation at higher purity and recovery specifications. The proposed model is solved at the desired purity and recovery specification of 90% for both i-BuOH and EtOH, respectively. The model consists of 506 equations and 495 variables (10 binaries) and is solved to global optimality within 240 s. The globally optimal network configuration is shown in Figure 5.

The optimal network incorporates three stages of Type B membrane and utilizes all four available stages of Type A membrane, requiring a total area of 1158.3 m^2. The higher permeance of EtOH in Type B membrane, compared to the permeance of i-BuOH in Type A membrane, facilitates the separation of EtOH as the initial step. Therefore, the fresh feed is fed to the sub-network with Type B membranes. As a result, EtOH is first separated and gets collected in the final permeate product in the sub-network with Type B membranes. In contrast, the final retentate product from the sub-network with Type B membranes, mainly comprising i-BuOH and H_2O, is subsequently fed to the sub-network with Type A membranes for the further separation of i-BuOH from the remaining aqueous mixture. Finally, i-BuOH is separated and collected as the final permeate product from the sub-network with Type A membranes, while the remaining aqueous mixture, predominantly

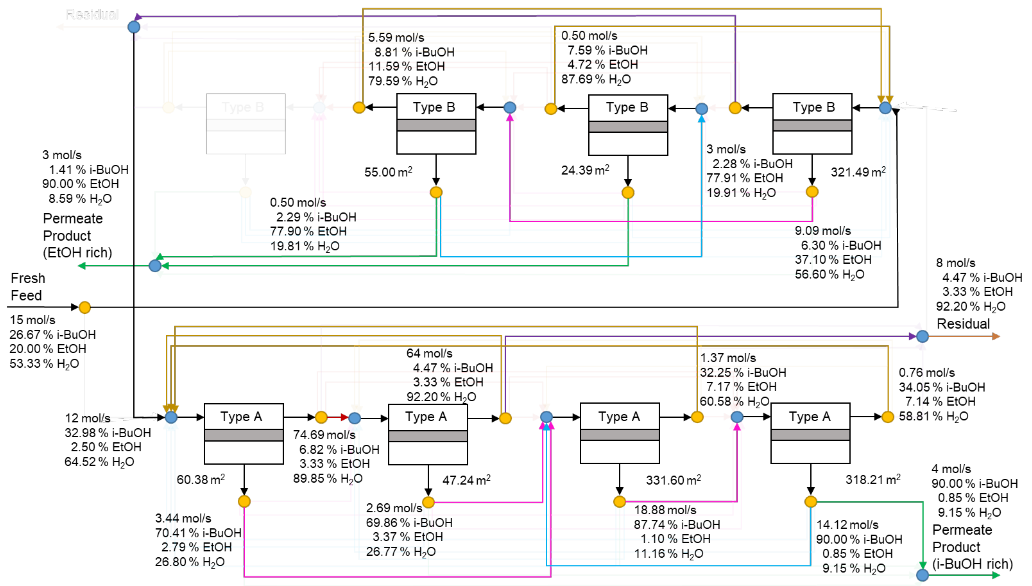

Figure 5: Two component separation: global optimal network to recover i-BuOH and EtOH at the desired recovery

containing H_2O, is collected as the residual.

CONCLUSIONS

In this study, we proposed an optimization model for membrane network synthesis tailored for the separation of multiple components from liquid mixtures. First, we developed a physics-based nonlinear surrogate model to describe pervaporation-based crossflow membrane permeation for liquid mixtures. Second, we proposed a comprehensive superstructure, incorporating multiple sub-networks, each with distinct membrane types, featuring multiple stages with rich stream interconnections. Third, we formulated a mixed-integer nonlinear programming model, integrating the two aforementioned elements, to determine the network configuration and operating conditions that minimize the overall network area. The proposed optimization model effectively identifies the global optimal network, as illustrated by the applications presented.

DIGITAL SUPPLEMENTARY MATERIAL

DAE unit model reformulation, simulation data, figures, and the mathematical formulation for the optimization model is presented in the Supplementary Material (LAPSE:2025.0008).

ACKNOWLEDGEMENT

This effort was funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under Award Number DE-EE0009494 and the Great Lakes Bioenergy Research Center, U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research under Award Number DE-SC0018409.

REFERENCES

1. H. Strathmann, Membrane separation processes, Journal of Membrane Science 9 (1981) 121–189. https://doi.org/10.1016/S0376-7388(00)85121-2.
2. L.M. Robeson, The upper bound revisited, Journal of Membrane Science 320 (2008) 390–400. https://doi.org/10.1016/j.memsci.2008.04.030.
3. P.F. Zito, A. Brunetti, G. Barbieri, Multi-step membrane process for biogas upgrading, Journal of Membrane Science 652 (2022) 120454. https://doi.org/10.1016/j.memsci.2022.120454.
4. I.E. Grossmann, Mixed-Integer Optimization Techniques for Algorithmic Process Synthesis, in: J.L. Anderson (Ed.), Advances in Chemical Engineering, Academic Press, 1996: pp. 171–246. https://doi.org/10.1016/S0065-2377(08)60203-3.
5. J. Marriott, E. Sørensen, A general approach to modelling membrane modules, Chemical Engineering Science 58 (2003) 4975–4990. https://doi.org/10.1016/j.ces.2003.07.005.
6. S. Weller, W.A. Steiner, Separation of Gases by Fractional Permeation through Membranes, Journal of Applied Physics 21 (1950) 279–283. https://doi.org/10.1063/1.1699653.
7. Y. Shindo, T. Hakuta, H. Yoshitome, H. Inoue, Calculation Methods for Multicomponent Gas Separation by Permeation, Separation Science and Technology 20 (1985) 445–459. https://doi.org/10.1080/01496398508060692.

8. J.K. Scott, P.I. Barton, Reachability Analysis and Deterministic Global Optimization of DAE Models, in: A. Ilchmann, T. Reis (Eds.), Surveys in Differential-Algebraic Equations III, Springer International Publishing, Cham, 2015: pp. 61–116. https://doi.org/10.1007/978-3-319-22428-2_2.
9. Z. Chen, M. Tawarmalani, R. Agrawal, Global minimization of power consumptions for multicomponent gas membrane cascades, Computers & Chemical Engineering 180 (2024) 108464. https://doi.org/10.1016/j.compchemeng.2023.108464.
10. G.S.P. Taifan, C.T. Maravelias, Generalized optimization-based synthesis of membrane systems for multicomponent gas mixture separation, Chemical Engineering Science 252 (2022) 117482. https://doi.org/10.1016/j.ces.2022.117482.
11. J.A. Chavez Velasco, R. Tumbalam Gooty, M. Tawarmalani, R. Agrawal, Optimal design of membrane cascades for gaseous and liquid mixtures via MINLP, Journal of Membrane Science 636 (2021) 119514. https://doi.org/10.1016/j.memsci.2021.119514.
12. R. Pathare, R. Agrawal, Design of membrane cascades for gas separation, Journal of Membrane Science 364 (2010) 263–277. https://doi.org/10.1016/j.memsci.2010.08.029.
13. R. Qi, M.A. Henson, Membrane system design for multicomponent gas mixtures via mixed-integer nonlinear programming, Computers & Chemical Engineering 24 (2000) 2719–2737. https://doi.org/10.1016/S0098-1354(00)00625-6.
14. A. Aliaga-Vicente, J.A. Caballero, M.J. Fernández-Torres, Synthesis and optimization of membrane cascade for gas separation via mixed-integer nonlinear programming, AIChE Journal 63 (2017) 1989–2006. https://doi.org/10.1002/aic.15631.
15. V.S.K. Adi, M. Cook, L.G. Peeva, A.G. Livingston, B. Chachuat, Optimization of OSN Membrane Cascades for Separating Organic Mixtures, in: Z. Kravanja, M. Bogataj (Eds.), Computer Aided Chemical Engineering, Elsevier, 2016: pp. 379–384. https://doi.org/10.1016/B978-0-444-63428-3.50068-0.
16. H. Verma, D. Jassby, C.T. Maravelias, Superstructure-based Optimization of Membrane Network Systems for Multicomponent Liquid Mixture Separation, Journal of Membrane Science (2024) 123574. https://doi.org/10.1016/j.memsci.2024.123574.
17. J.G. Wijmans, R.W. Baker, The solution-diffusion model: a review, Journal of Membrane Science 107 (1995) 1-21. https://doi.org/10.1016/0376-7388(95)00102-I
