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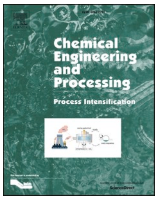

Next-generation pervaporation-assisted distillation: Recent advances in process intensification

Maria Polyakova [a], Mirko Skiborowski [b,*]

[a] Laboratory of Fluid Separations, Ruhr Universität Bochum, Bochum, Germany
[b] Institute of Process Systems Engineering, Hamburg University of Technology, Hamburg Germany

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ABSTRACT

Pervaporation is a well-established membrane separation process that effectively overcomes limitations of distillation due to azeotropes and distillation boundaries. The selective mass transfer of pervaporation membranes has enabled successful implementation in a variety of industries, with applications in the chemical industry, as well as the food and pharma industry, including membrane bioreactors in fermentation processes. Yet, the majority of applications in separation processes remain focused on the dehydration of aqueous-organic process streams, including biofuel and bioethanol production. Pervaporation-assisted distillation processes leverage the benefits of both technologies and exploit the resulting synergies to provide energy and cost-efficient separations, especially for azeotropic mixtures, which otherwise require rather energy intensive distillation processes, such as pressure-swing, extractive or hetero-azeotropic distillation. The current review provides an overview of recent developments that enable further process intensification of pervaporation-assisted distillation processes and provides some perspective on emerging trends that may result in a wider application of these interesting hybrid separation processes.

1. Introduction

The chemical industry is currently undergoing a period of transformation, driven by rapidly evolving markets, increasing global competition, rising energy costs, and growing sustainability pressures. The shift toward more sustainable chemical processes necessitates an expanded toolbox for process development beyond conventional unit operations. This includes the exploration of novel solvents, alternative raw materials, and intensified hybrid separation techniques.

One of the key challenges in this evolving landscape is the energy-intensive nature of thermal separation processes, which account for approximately 30–80 % of the total energy consumption in the production of bulk and specialty chemicals. Distillation alone is estimated to consume about one million barrels of crude oil per day in North America alone [1]. Notably, distillation accounts for approximately 40 % of the energy used in the chemical industry [2]. Given the widespread use of distillation, even smaller improvements in energy efficiency can result in substantial cost savings and environmental benefits [3]. Given the high energy demand of the chemical industry, there is a significant opportunity to enhance efficiency, particularly in the processing of organic solvents, many of which form azeotropic mixtures with water.

The integration of energy-saving technologies, such as membrane processes, has the potential to drastically reduce energy consumption [4]. So far, mostly pervaporation (PV), vapor permeation (VP), and nanofiltration have been explored in membrane-assisted distillation processes [5], whereas PV and VP-assisted distillation processes are the most widely investigated and industrially applied [6]. Recent advancements in pervaporation-assisted distillation have opened new avenues for process intensification, enabling improved separation performance, reduced energy consumption, and greater integration into existing industrial frameworks. The current work provides a comprehensive review of these developments, discussing key innovations, emerging applications, and future perspectives on the role of pervaporation in next-generation hybrid separation processes.

Advancements in membrane materials and module designs have further propelled the application of pervaporation in industrial settings. Innovations in membrane fabrication have led to improved selectivity and permeability, enhancing the performance of pervaporation systems. These developments have expanded the applicability of pervaporation-assisted distillation processes, making them viable for a broader range of separations.

By combining the high capacity and separation efficiency of

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* Corresponding author.
E-mail address: mirko.skiborowski@tuhh.de (M. Skiborowski).

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distillation with the selective permeation offered by pervaporation, hybrid processes can achieve more efficient separations that would otherwise be challenging or impossible by the individual unit operations alone [7]. While pervaporation struggles to preform sharp splits for a given mixture due to vanishing driving forces, it provides superior separation performance compared to distillation particularly for azeotropic or close-boiling mixtures. Hybrid processes based on the integration of both unit operations enable a preferential operation of the individual unit operations for conditions with sufficient driving forces [8,9]. The benefits of basic pervaporation-assisted distillation processes are best illustrated for binary systems in classical yx-diagrams, as represented in Fig. 1. The shaded areas in these diagrams highlight the composition range in which the pervaporation membranes are operated, while the remaining part of the diagram is covered by distillation columns. The respective pervaporation-assisted distillation configurations are depicted directly below the yx-diagrams. These configurations allow separations in narrow-boiling and azeotropic regions, in which a separation by means of distillation is infeasible or only feasible as significant reflux ratios and energy requirements. The left diagram and the below process illustrate how the pervaporation membrane can be utilized for the intensification of a distillation process for a close boiling mixture, for which the membrane does not need to be highly selective. While distillation columns require high reflux ratios and numerous equilibrium stages for the separation of such narrow boiling mixtures with relative volatilities close to one, the hybrid separation process can leverage the higher selectivity of the membranes separation to perform the bulk separation efficiently, while distillation ensures the final purification to achieve high product purities, optimizing both energy efficiency and separation performance. The illustration in the center of Fig. 1 illustrates the separation of an azeotropic mixture with a low boiling azeotrope close to one of the pure components, such as the case for ethanol dehydration. The pervaporation membrane purifies the top product of the distillation column, while recycling a concentrated retentate further away from the azeotropic composition back to the distillation column, which purifies the bottom product. For azeotropic mixture in which the azeotrope is located further away from the pure components, as e.g. for isopropanol dehydration, the right process configuration in Fig. 1 with two columns and an intermediate pervaporation stage can be a proficient hybrid configuration. The hybrid process performs the purification of both products by the individual distillation columns, while the intermediate membrane separation breaks the azeotrope. Roth et al. [10] and Lutze and Górak [11] provide a more elaborate comparison of the merits of the standalone processes and the benefits of the hybrid configurations.

As summarized by Górak et al. [13] and Lutze and Górak [11], the primary application of membrane-assisted distillation processes in general lies in the dehydration of organic solvent, with the majority of applications in the purification of alcohols, especially ethanol and isopropanol. Other application areas include the purification of higher alcohols (such as butanol and pentanol), ketones (e.g., acetone [14]), nitriles, such as acetonitrile [15]), esters, including methyl, ethyl, and butyl acetate [16,17], as well as n-propyl propionate [18], and ethers such as MTBE [19], ETBE [20], TAEE [21], and THF [22]. An earlier elaborate review on the research on pervaporation-assisted separation processes until 1999 was given by Lipnizki et al. [23], while some experience from industrial applications is described in the work of Maus and Brüschke [24] and Roza and Maus [25], as well as the textbooks of Basile et al. [26]. In a more recent book chapter, Baig [27] reports on a number of different industrial applications of *PetroSeps Azeo-Sep*® and *VOC-Sep*® pervaporation membranes, providing several illustrations of the respective implementations ranging from 5.000–50.000 t/y, while Liu et al. [6] provide an extensive more recent review on pervaporation and vapor permeation-assisted distillation processes, including industrial applications in China, showcasing the practical relevance of hybrid processes beyond academic research. While the primary application of pervaporation-assisted distillation remains the dehydration of aqueous-organic process streams, where the most significant use is in biofuel production, particularly bioethanol, pervaporation is also employed for separating methanol from organic components like MTBE, methyl acetate, THF, and toluene. Emerging applications include solvent purification in extractive distillation and process intensification in reactive distillation, particularly for esterification, etherification, and transesterification reactions involved in producing ethyl acetate, butyl acetate, butyl ether, DMC, ETBE, and TAME.

The current review focusses on the most recent developments for hybrid pervaporation-assisted distillation processes published in the recent decade. As a baseline information Section 2 first provides an overview of current technology providers for pervaporation membranes and remaining development issues. Recent developments in pervaporation-assisted distillation are further discussed in Section 3. At first predictive modeling for pervaporation processes is addressed in Section 3.1, while new modeling and conceptual design approaches are summarized in Section 3.2. Section 3.3 explores innovative methods for analyzing energy efficiency and designing intensified pervaporation-assisted distillation processes. Sections 3.4 and 3.5 analyze the recent developments on pervaporation-assisted extractive distillation and reactive distillation, respectively. While most of these investigations focus solely on conceptual design studies, Section 3.6 summarizes the recent work on studies that include experimental investigations. Section 3.7 concludes the technical discussion by examining recent advancements in the integration of pervaporation-assisted distillation within a single intensified equipment. Finally, Section 4 presents the overall conclusions of the study and outlines key recommendations for future research and development efforts aimed at facilitating the industrial implementation of pervaporation-assisted distillation processes.

2. Technology providers for pervaporation membranes and development issues

A variety of vendors offer commercially available polymeric and inorganic membranes for pervaporation, including organophilic membranes, while the majority of membranes are hydrophilic with major applications in solvent dehydration. Membrane technology for pervaporation has seen significant advancements across North America, Europe, and Asia, with various vendors specializing in different materials, focusing on membrane performance and industrial applications.

In North America, companies such as *Ardent* (formerly *Compact Membrane Systems*)[1] and *Celazole PBI*[2] focus on advanced polymeric membranes with high thermal stability and chemical resistance, targeting applications like organic solvent separations and azeotropic mixtures. *Ardent* manufactures perfluoropolymer-based pervaporation membranes that are compatible with a wide range of chemicals, resistant to surface fouling, and perform well at high temperature. *Celazole PBI* is the world's sole commercial producer of poly-2,2′-(m-phenylene)-5,5′-bibenzimidazole (PBI), a glassy thermoplastic known for its exceptional thermal stability (up to 427 °C) and broad chemical resistance, with PBI-based pervaporation membranes designed for the production and recycling of organic chemicals. *GMM Pfaudler*[3] has incorporated *Hydro Air Research Italia*, offering pervaporation membranes for organic solvent drying and concentration processes. *PetroSep*[4] is based in Canada and offers the *VOC-SEP*™ and *AZEO-SEP*™ pervaporation membranes primarily used for petrochemical applications, as well as other applications, with some illustrations provided by Baig [27]. *PetroSep* also holds a patent on membrane-assisted fluid separation [28]

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[1] https://www.ardenttechnologies.com/

[2] https://pbipolymer.com/markets/membrane/

[3] https://www.gmmpfaudler.com/membrane-separation-systems-1/membrane-separation-solutions/other-separation-solutions/pervaporation-1

[4] https://petrosep.com/membrane-technologies/#1627924373400-e87a0041-f157

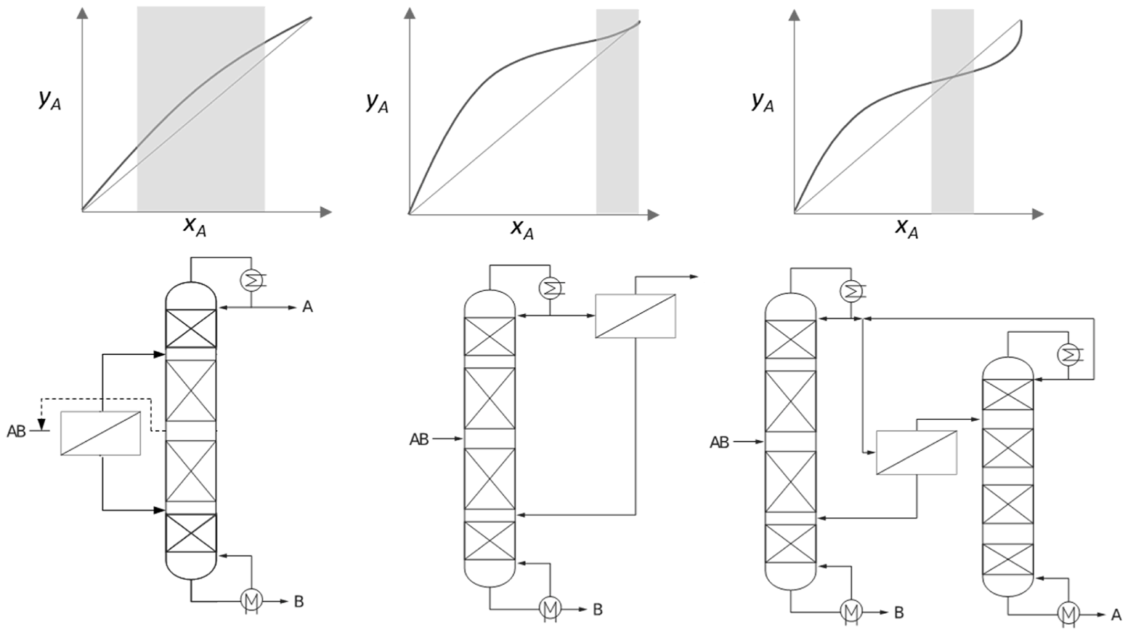

Fig. 1. Illustration of potential pervaporation-assisted hybrid distillation processes for the separation of azeotropic and close boiling mixtures, similar to the presentation by Skiborowski and Górak [12].

(WO2003000389A3). Whitefox,[5] is one of the largest vendors of pervaporation and vapor permeation membranes with several large-scale bioethanol plants, with branches in the U.S., Canada, and the UK. Whitefox has filed various patents for membrane-based solutions for bioethanol production tailored for process integration and efficiency in recent years [29–32](US 10,486,079; US 11,426,675; US20240033652A1; US20240140893A1) .

In Europe, membrane development is driven by a combination of large-scale industrial players and research-based organizations. *BORSIG GmbH*,[6] including *GMT Membrantechnik*, focuses on solvent dehydration applications, such as ethanol isopropoanol. BORSIG GmbH hold a patent on oxygen separation with composite ceramic hollow fibers membranes [33] (EP1846345B1). *PolyAn*[7] is another German company that offers advanced polymer membrane technology with specialization in molecular surface engineering for organophilic separations, providing tailored solutions. PolyAn holds a patent for organophilic pervaporation [34] (EP2734288A1). *DeltaMem AG*[8] in Switzerland is one of the largest vendors offering vapor permeation and pervaporation solutions for pharmaceutical and fine chemical industries, after the acquisition of Sulzer's membrane technology business. In The Netherlands, *Pervatech*[9] and *TNO*[10] (formerly *ECN*) provide high-performance ceramic, polymer and hybrid silica membranes, respectively, catering to diverse industrial needs. Peravatech membranes and engineered pervaporation processes are also offered in the U.S. by *Artisan Industries Inc.*[11] *TNO* is an independent statutory research organization in The Netherlands that focuses on applied science, which has developed a particularly effective and stable hybrid silica membrane that is also offered by *Pervatech. VITO*[12] is an independent research and technology organization in Belgium, that develops functionalized ceramic membranes for organophilic separations, including custom surface modifications, with research activities on hybrid separation processes and pilot-scale implementation.

Asia has also become a major hub for membrane manufacturing and application, with several companies offering membranes for pervaporation in China and Japan. *Jiangsu Long Membrane Hi-tech*,[13] collaborating with the Membrane Science and Technology Research Institute of Nanjing University of Technology, and *Jiuwu Hi-Tech*[14] are both located in Nanjing, offering high-performance polymeric and ceramic membranes [35] (CN105130441B), supporting the growth of pervaporation technologies in China. Jiuwu Hi-Tech holds a patent on zero-discharge nanofiltration membrane for high salt wastewater (CN108623104B). *MegaVision*[15] in Shanghai has pioneered osmotic distillation and offers pervaporation membranes using proprietary polymer blends using PS, PES, PVDF, PAN, PP, PEK, PTFE, PDMS, and PMP polymers. *Tangent (TFTFluid)*[16] has according to own information deployed over 300 pervaporation plants utilizing zeolite membranes for solvent dehydration. In Japan, *Mitsubishi Chemical Group*[17] has developed ZEBREX™ zeolite pervaporation membranes, which are employed in industrial solvent dehydration and organic separation applications.

Fig. 2 provides an overview of key industrial players involved in pervaporation technology, categorized by geographic region (Europe, America, and Asia). The table highlights the services and products offered by each company in three main areas: production facilities, module manufacturing, and membrane fabrication. The presence, absence, or lack of information for each item is indicated using a standardized legend. Additionally, the official website for each company is listed to facilitate further reference. This compilation serves as a baseline for identifying potential industrial vendors and service providers, further providing an overview on the current global distribution of expertise in pervaporation technology.

Apart from the available technology providers a wide number of

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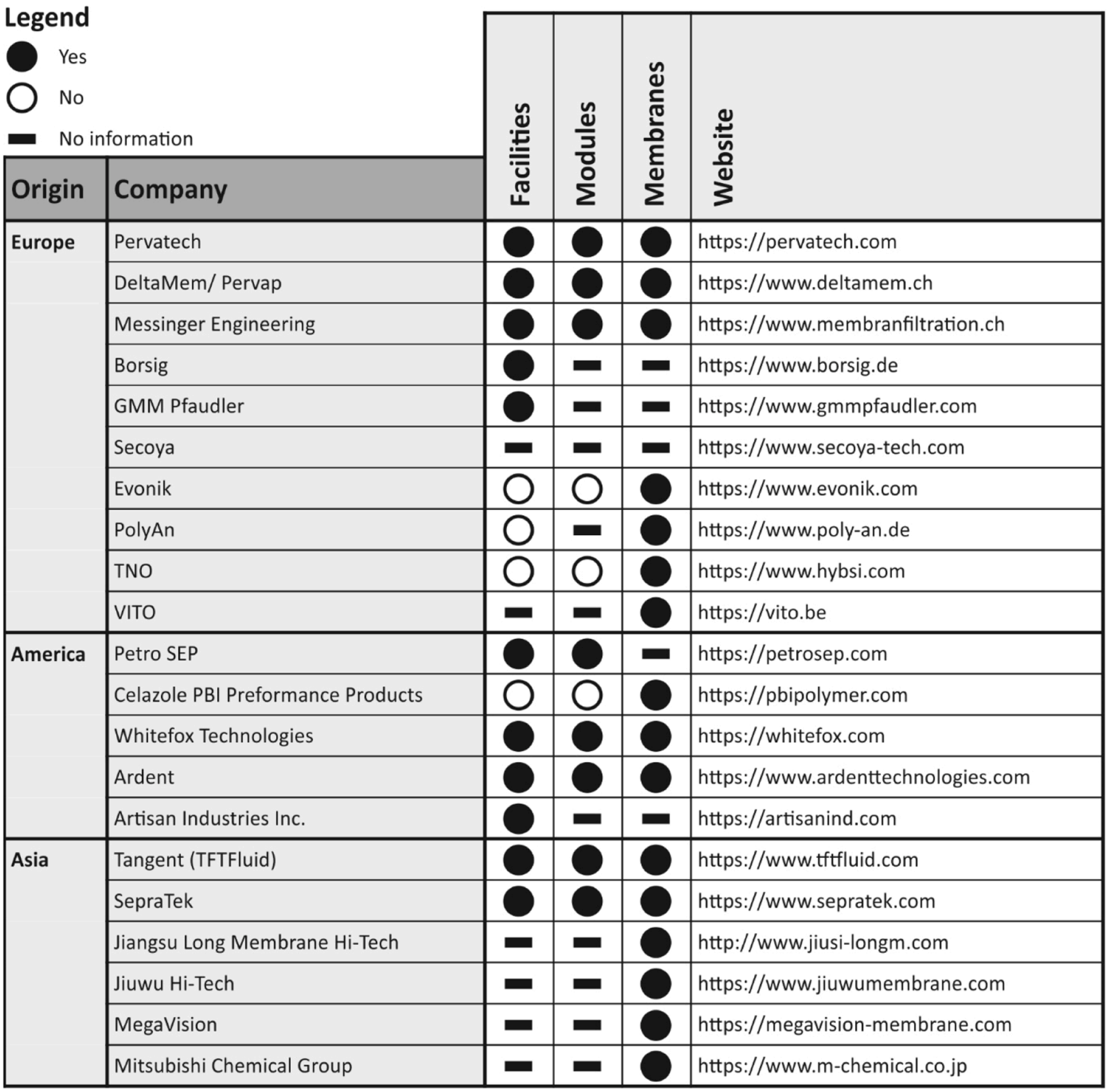
[5] https://whitefox.com/
[6] https://www.borsig.de/en/products-and-services/membrane-technology-for-liquid-separation/pervaporation
[7] https://www.poly-an.de/
[8] https://www.deltamem.ch/
[9] https://pervatech.com/
[10] https://www.hybsi.com/
[11] https://artisanind.com/equipment/pervaporation-membrane-modules/
[12] https://vito.be/en/applications/membrane-technology
[13] http://www.jiusi-longm.com/
[14] https://www.jiuwumembrane.com/
[15] https://megavision-membrane.com/about-us.html
[16] https://www.tftfluid.com/products/pv-vp-membrane-for-dehydration.html
[17] https://www.m-chemical.co.jp/en/products/departments/mcc/ion/product/1201038_8072.html



Legend
● Yes
○ No
▬ No information

Origin	Company	Facilities	Modules	Membranes	Website
Europe	Pervatech	●	●	●	https://pervatech.com
	DeltaMem/ Pervap	●	●	●	https://www.deltamem.ch
	Messinger Engineering	●	●	●	https://www.membranfiltration.ch
	Borsig	●	▬	▬	https://www.borsig.de
	GMM Pfaudler	●	▬	▬	https://www.gmmpfaudler.com
	Secoya	▬	▬	▬	https://www.secoya-tech.com
	Evonik	○	○	●	https://www.evonik.com
	PolyAn	○	▬	●	https://www.poly-an.de
	TNO	○	○	●	https://www.hybsi.com
	VITO	▬	▬	●	https://vito.be
America	Petro SEP	●	●	▬	https://petrosep.com
	Celazole PBI Preformance Products	○	○	●	https://pbipolymer.com
	Whitefox Technologies	●	●	●	https://whitefox.com
	Ardent	●	●	●	https://www.ardenttechnologies.com
	Artisan Industries Inc.	●	▬	▬	https://artisanind.com
Asia	Tangent (TFTFluid)	●	●	●	https://www.tftfluid.com
	SepraTek	●	●	●	https://www.sepratek.com
	Jiangsu Long Membrane Hi-Tech	▬	▬	●	http://www.jiusi-longm.com
	Jiuwu Hi-Tech	▬	▬	●	https://www.jiuwumembrane.com
	MegaVision	▬	▬	●	https://megavision-membrane.com
	Mitsubishi Chemical Group	▬	▬	●	https://www.m-chemical.co.jp

Fig. 2. Overview over the key companies in pervaporation technology.

research institutes work on the development of advanced membranes and process concepts. The interested reader is referred to the excellent recent review papers from Ong et al. [36], which provides a detailed overview on membrane materials and fabrication methods and Liu et al. [37], which focus on innovative membrane materials like mixed-matrix membranes and emerging two-dimensional materials. Vane [38] provides a review of membrane materials particularly for the dehydration of organic solvents, whereas the review of Liu et al. [39] focusses on materials for organic solvent separations by pervaporation and vapor permeation. The even more specific review of Imad and Castro-Munoz [40] focusses particularly on ethanol dehydration, while the review of Castro Munoz [41] focusses on desalination applications with pervaporation membranes. Finally the review paper of Xu et al. [42] focusses specifically on metal-organic framework (MOF)-based membranes and the review paper of Ehsani et al. [43] focus on biodegradable membranes with antifouling properties, considering the end-of-life treatment of used membranes.

As pointed out by van der Bruggen and Luis [44] the development of novel membrane materials with improved separation performance and stability at the laboratory scale is extensive, but many of these innovations remain far from practical industrial implementation. Most commercially available membranes continue to be based on well-established polymers, enhanced through crosslinking and surface modifications, or on inorganic materials such as zeolites. The following item list summarizes a few remaining technology development issues that present challenges for the application of pervaporation (assisted) processes, based on the development of the membrane technology itself, while the subsequent section focusses in detail on the current state and recent developments for advanced process concepts and efficient process design. The remaining membrane limitations that are primarily related to the specific membrane material and the design of the modules in operation can be summarized as follows:

- Limited selectivity and temperature resistance of polymeric membrane

Available polymeric membranes like Polyvinyl alcohol (PVA), Polyamid (PI), Polyacrylic acid (PAA), Polyacrylnitril (PAN), Chitosan, Cellulose-based or Amorphos perfluoropolymers (APFPs). There are reviews available like [45,46]. Polymeric membranes are generally cheaper than inorganic membranes, but they generally exhibit lower flux and selectivity. They are also limited in thermal stability, with temperature limitations in the range of 100 °C [47], reaching > 400 °C in exceptional cases (see above information for *Calzone PBI*). While this limitation directly affects the achievable flux, which approximately doubles for each 20 K increase in feed temperature [47], it is also a limiting factor for high-temperature applications. Current developments to advance the limits of existing polymeric membranes include the development of advanced membrane materials, including microporous polymers, mixed-matrix, MOF-based membranes [39,42] and other 2D materials and surface modifications [37], using experimental design and computational methods for optimized material discovery, such as quantitative structure–performance relationships [40]. Other developments focus on decreasing the costs of inorganic membranes. Based on advanced manufacturing methods, potentially leveraging additive manufacturing techniques to reduce production costs.

- Membrane aging and fouling

Fouling reduces membrane performance by limiting mass transfer and selectivity, necessitating periodic cleaning or membrane replacement. Membrane aging and fouling contribute to a shortened lifespan, leading to increased operational costs and material waste. One possible solution is the development of anti-fouling membrane materials with improved surface properties to minimize fouling and extend operational life. Enhanced material compositions and surface modifications can increase resistance to degradation and fouling and improve membrane durability.

- Swelling-induced selectivity loss in pervaporation membranes

Swelling is a critical limitation in pervaporation membranes, particularly during the separation of organic–organic or organic–water mixtures where strong sorption of penetrant molecules can cause physical expansion of the polymer matrix. Commonly used materials such as Polyvinyl alcohol (PVA), Polydimethylsiloxane (PDMS), and Polyimide (PI) show varying degrees of swelling depending on feed composition and operating conditions. This leads to changes in free volume and polymer chain mobility, negatively impacting selectivity and sometimes causing mechanical degradation over time. For example, hydrophilic membranes used for dehydration of alcohols may swell excessively in the presence of water, resulting in a loss of water–organic selectivity. Swelling can also cause plasticization, where the membrane becomes too flexible, further impairing its separation performance. Strategies to mitigate this effect include chemical crosslinking, incorporation of inorganic fillers (e.g., zeolites, MOFs), and the development of mixed-matrix or hybrid membranes that exhibit reduced swelling while maintaining high flux [48]. Computational modeling and experimental sorption–diffusion studies are increasingly used to predict and design membranes with controlled swelling [5]. This is essential to ensure long-term stability and performance in pervaporation systems.

- Sustainable end-of-life treatment and recycling strategies

The disposal of used membranes poses environmental concerns, necessitating the development of recycling or sustainable disposal strategies. While this issue is comparable small at current state, an increased utilization of membrane processes will unavoidably result in an increased number of end-of-life membranes that need to be treated. Therefore, it is crucial that recycling methods for membrane materials are established and potentially considered during membrane development, e.g. for biodegradable membranes [43], in order to reduce waste and improve the sustainability of membrane processes. This also includes the consideration of the sustainability of the materials used during membrane manufacture [49].

- Heat-management concepts for advanced membrane modules

As already mentioned, the flux depends strongly on temperature, which drops continuously in classic modules without specific heating, due to the evaporation of the permeating molecules. While some concepts for heated modules towards an isothermal operation have been developed [50,51] the design and manufacture of specialized membrane modules that integrate membrane permeation with effective heat recovery and management provides an important lever to improve energy efficiency.

The different advantages and disadvantages of specific materials, are summarized in Fig. 3. It presents a comparative assessment of various membrane materials used in pervaporation, categorized by material type: polymeric, microporous, layered, mixed-matrix, and 2D-materials. The evaluation includes key performance and operational parameters such as permeance (G), selectivity, maximum operating temperature (°C), maximum water content tolerated in the feed (% H_2O), operational pH range, and material availability. Performance indicators are rated as good, bad or not assessable, based on current literature and industrial data. This comparative overview supports the selection of membrane materials based on specific separation tasks and operating conditions in pervaporation processes and highlights the ongoing need for material innovation to expand the applicability of pervaporation in industrial separation challenges.

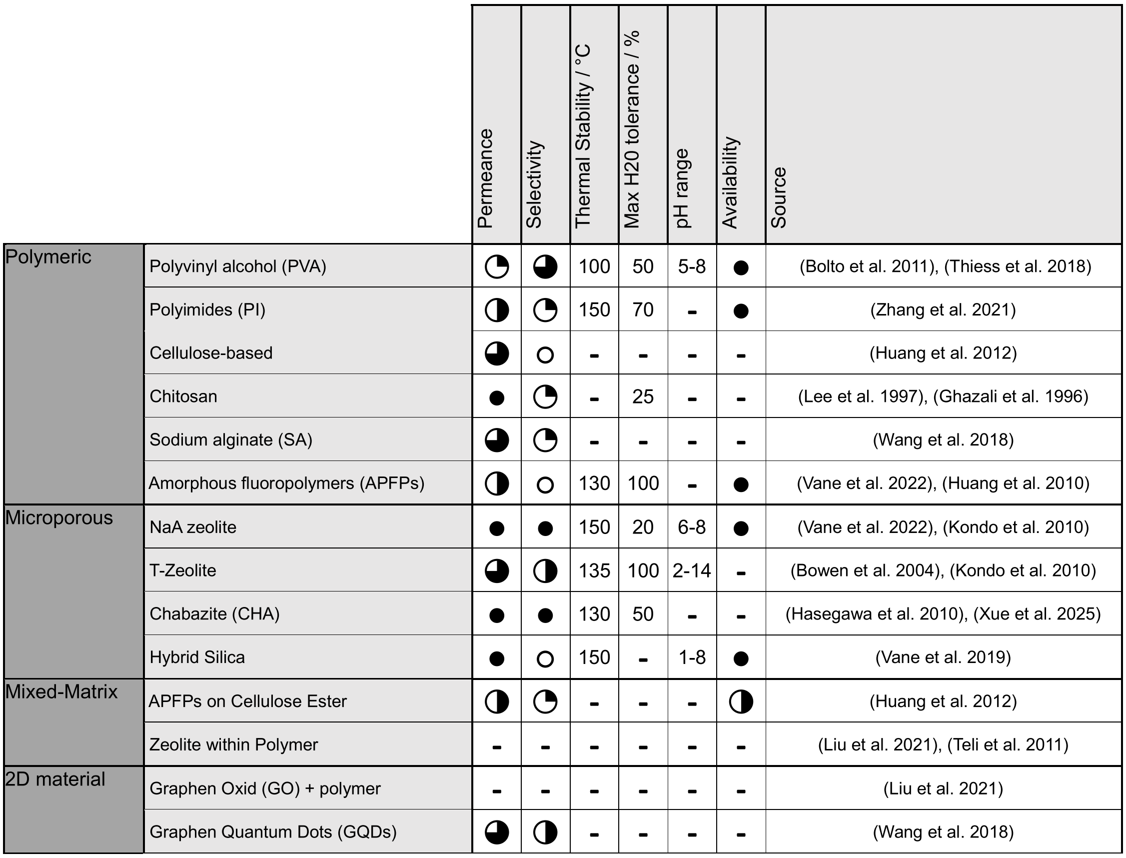
While van der Bruggen and Luis [44] emphasize that advancements to overcome these limitations are critical, especially for the establishment of organophilic separations, they also highlight the necessity of systems engineering and seamless integration of pervaporation into the chemical engineering toolbox as key factors in achieving a breakthrough for broader industrial applications. In this spirit, the following section focusses on the recent advances of pervaporation-assisted distillation processes in specific, covering both process concepts as well as methods and models for process development and further process intensification.

3. Recent developments for pervaporation-assisted distillation

Over the past decade, numerous conceptual design studies have explored the integration of pervaporation and distillation processes, with a larger focus on extractive and reactive distillation processes. These studies have demonstrated potential energy and cost savings of 10–30 %, depending on the specific application and the extent of additional energy integration. To maximize its efficiency, process design studies have incorporated different heat integration strategies, including thermal coupling and heat pump utilization. However, these additional complexities further challenge the development of integrated process concepts, necessitating advanced tools for process design and optimization. Beyond process design optimization, research efforts also focus on improving membrane models and developing predictive tools for membrane performance. Both aspects are crucial for incorporating pervaporation into the standard toolkit of chemical engineers and solidifying its role in the conceptual design of distillation-based separation processes. Finally, also novel developments in respect to equipment integration in the concept of a hybrid distillation-pervaporation in a single unit (DPSU) have been made and first proposed by the group of Fontalvo [52]. The different research areas are further explored and the results discussed in more detail in the subsequent subsections.

3.1. Predictive modeling for pervaporation processes

As most research publications on pervaporation-assisted distillation processes are based on computational studies the availability of sufficiently accurate models is a prerequisite for a reliable assessment of the performance of the hybrid processes. Distillation columns can readily be modeled by existing modules in basically every commercial flowsheet simulator, building on established equilibrium-tray or rate-based models. These models can readily be applied to various chemical systems, building either on the existing databases for pre-defined parameters for the underlying thermodynamic models, or predictive models, such as the well-known group-contribution models [53], or more



		Permeance	Selectivity	Thermal Stability / °C	Max H20 tolerance / %	pH range	Availability	Source
Polymeric	Polyvinyl alcohol (PVA)	◔	◕	100	50	5-8	●	(Bolto et al. 2011), (Thiess et al. 2018)
	Polyimides (PI)	◑	◔	150	70	-	●	(Zhang et al. 2021)
	Cellulose-based	◕	○	-	-	-	-	(Huang et al. 2012)
	Chitosan	●	◔	-	25	-	-	(Lee et al. 1997), (Ghazali et al. 1996)
	Sodium alginate (SA)	◕	◔	-	-	-	-	(Wang et al. 2018)
	Amorphous fluoropolymers (APFPs)	◑	○	130	100	-	●	(Vane et al. 2022), (Huang et al. 2010)
Microporous	NaA zeolite	●	●	150	20	6-8	●	(Vane et al. 2022), (Kondo et al. 2010)
	T-Zeolite	◕	◑	135	100	2-14	-	(Bowen et al. 2004), (Kondo et al. 2010)
	Chabazite (CHA)	●	●	130	50	-	-	(Hasegawa et al. 2010), (Xue et al. 2025)
	Hybrid Silica	●	○	150	-	1-8	●	(Vane et al. 2019)
Mixed-Matrix	APFPs on Cellulose Ester	◑	◔	-	-	-	◑	(Huang et al. 2012)
	Zeolite within Polymer	-	-	-	-	-	-	(Liu et al. 2021), (Teli et al. 2011)
2D material	Graphen Oxid (GO) + polymer	-	-	-	-	-	-	(Liu et al. 2021)
	Graphen Quantum Dots (GQDs)	◕	◑	-	-	-	-	(Wang et al. 2018)

Fig. 3. Overview of specific advantages and disadvantages of different types of membrane materials (in order ○◔◑◕● with ○ = low and ● = high, - = no info).

recently proposed prediction on the basis of machine learning models [54–56].

Unlike distillation columns, membrane separations in general, and specifically pervaporation modules mostly need to be built as custom models [7]. Kancherla et al. [57] provide an elaborate overview of the different capabilities and options for modeling membrane separations and the different approaches presented in different publications for modeling and simulation of pervaporation-assisted distillation processes. These models usually build on experimentally determined semi-empirical correlations for the local flux, which in most cases are based on the solution-diffusion model, assuming a dense membrane [26]. For modeling the performance of individual membrane modules usually some discretization scheme is applied, considering mass and energy balances, as well as potentially driving-force limiting effects and hydrodynamics [58,59]. These grey-box models are further combined with the established models for distillation columns, which usually build on the equilibrium stage models [57]. Consequently, the evaluation of pervaporation-assisted distillation processes usually requires a first experimental screening and initial characterization of a suitable membrane for a specific separation problem, representing a considerable burden compared to the easy evaluation of distillation processes, including azeotropic distillation processes, such as pressure-swing or extractive distillation. In order to overcome this limitation, predictive modeling of the separation performance of pervaporation membranes is required. Various computational approaches, including molecular simulations and machine learning techniques, have recently been investigated to predict membrane behavior, optimize material selection, and accelerate process design.

Molecular simulation does not only allow for the prediction of the separation performance of certain membrane materials, but also provides a fundamental understanding of membrane behavior at the atomic and molecular scales. It therefore enables researchers to analyze separation mechanisms and optimize membrane materials. Gupta et al. [60] have established a molecular simulation protocol for pervaporation processes, demonstrating the accuracy of atomistic models in predicting transport properties for desalination and ethanol-water separation. Similarly, Shan et al. [61] employed molecular dynamic simulations to study the effect of vinyl group modifications on polydimethylsiloxane (PDMS) membranes for furfural recovery, revealing how chemical modifications influence membrane performance. Anashkin et al. [62] extended these efforts by developing a tailored simulation approach for polyurethane membranes, incorporating macromolecular formation mechanisms and precise intermolecular interaction parameters to enhance accuracy in modeling pervaporation processes. Despite the huge potential of such molecular simulations their application for the development and design of pervaporation-assisted processes is likely limited, due to the large computational effort for performing such simulations.

As an alternative approach to predictive modeling machine learning (ML) has emerged as a powerful tool for predicting membrane performance, screening new materials, and optimizing membrane processes. For the separation of organic mixtures first developments on predictive data-driven models have been demonstrated for organic solvent nanofiltration [63–66]. The possibilities of such methods have been discussed most recently by Ignaz et al. [67] and Piccard et al. [68]. These works point out the importance of collective databases, which should comply with the FAIR principles [69]. Such a database was recently established for organic solvent nanofiltration [70] providing a foundation for the future development of predictive data-driven models for a wider set of membranes.

While such a database and a wider set of data-driven models is still lacking for pervaporation, first efforts have been made to showcase the potential of ML for pervaporation. Wang et al. [71] developed ML models using a dataset of 681 samples for water/ organic mixtures, allowing for high-throughput screening of polymer membranes and identifying ten promising candidates with enhanced separation capabilities. Yang et al. [72] further advanced ML-based pervaporation predictions by constructing models that predict separation factors for acetic acid-water systems based on polymer properties, membrane morphology, fabrication parameters, and operating conditions.

ML-based models are also used for polymer membrane design. Yang et al. [73] employed ML models to screen approximately one million hypothetical polymers, identifying high-performance materials with superior permeation separation indices and synthetic accessibility. This approach significantly reduces reliance on traditional trial-and-error methods, improving efficiency and cost-effectiveness in membrane development.

Osman et al. [74] provided a broader review of ML applications in membrane science, highlighting its role in energy production, gas separation, and water treatment, including pervaporation applications. In their perspective paper, Ignacz et al. [67] underscore the transformative potential of ML-based models in improving membrane efficiency and accelerating material discovery. They further highlight the potential of ML-based surrogate models that can be integrated to hybrid mechanistic-data-driven models, in order to integrate the accuracy of computationally expensive high-fidelity models. Such a synergy was also described by Xu et al. [75] for the integration of ML and molecular simulations for the design of polymeric membranes, focusing on OSN. Such an integration of molecular simulations and ML may also lead to future advances in generating predictive models for pervaporation, which would also benefit from an openly available community database in accordance with the FAIR principles, similar to OSN. Continued research in these areas will be crucial for realizing next-generation pervaporation membranes and expanding their industrial applicability.

3.2. *Novel modeling and conceptual design approaches for pervaporation-assisted distillation processes*

The integration of distillation and pervaporation in hybrid separation processes has gained significant attention due to its potential for enhanced separation efficiency and energy savings. Skiborowski et al. [7,76] provide an elaborate summary of the different methods for the generation of process variants, shortcut screening methods and optimization-based design methods which were proposed until 2014. This section therefore focusses on the recent developments that have been introduced in the last decade concerning novel modeling and design approaches to optimize these processes, incorporating conceptual models, simulation techniques, and process intensification strategies.

While the synthesis of process variants for pervaporation-assisted distillation mostly relies on manual configurations based on the analysis of thermodynamic criteria, such as the thermodynamic insight approach proposed by Jaksland and Gani [8], or the analysis of residue curve maps [12], several methods towards an automatic generation of process configurations have been proposed. Holtbrügge et al. [77] proposed a conceptual design approach that integrates the thermodynamic insight approach with an algorithmic framework generating feasible distillation-pervaporation configurations. Babi et al. [78] further introduced a three-stage workflow for the synthesis and design of intensified processes, enabling the development of pervaporation-assisted distillation systems. Their methodology, which combines a superstructure-based optimization of phenomena building blocks, based on simplified models, and subsequent simulation-based assessment with detailed flowsheet models, was exemplified through the synthesis of dimethyl carbonate (DMC) via transesterification of propylene carbonate and methanol. This approach underscores the role of systematic intensification strategies in enhancing process sustainability, which was further developed by Garg et al. [79] and is implemented in the tool ProCAFD offered by PSEforSPEED.[18] Alternative approaches aiming at a direct model-based synthesis of pervaporation-based and pervaporation-assisted distillation processes have been presented by Demirel et al. [80] and Kuhlmann et al. [81]. The chessboard-like building block superstructure model of Demirel et al. [80] allows for a generic combination of discrete mass-transfer elements and therefore an automated staging and definition of flow directions, which was demonstrated for different membrane processes. The state-space superstructure optimization approach of phenomena-based of Kuhlmann et al. [81], rather considers larger pre-confected building blocks, representing either individual sections of a distillation column or membrane modules. The method was demonstrated for ethanol dehydration as well as a more complex example for DMC synthesis with vapor permeation-assisted reactive distillation [82].

Most conceptual design studies focus either on a simulation-based assessment, that either preforms a manual, or sensitivity study based assessment, or exploits an active interface to perform a simulation-based optimization of pervaporation-assisted distillation processes [57], superstructure-based optimization approaches have been proposed already in the 2000s by Kookos [83] and Barakat and Sørensen [84] for the design of pervaporation-assisted distillation processes. The process models for these design studies generally rely on some simplifications. While e.g. the superstructure methods of Skiborowski et al. [76] and Chia et al. [85] are capable to automatically determine the number, size and operating conditions of individual membrane stages, as illustrated in Fig. 4 driving force limiting effects, such as pressure drop, or concentration and temperature polarization as frequently neglected in these models, as they do not consider a fixed membrane module design. These simplifications are reasonable when focusing on the selection of the most promising process concept from a pool of potential options, but result in a potentially too optimistic design for a final implementation.

In order to provide a more-detailed design of a pervaporation-assisted distillation process Sosa et al. [86] developed a simulation-based framework for bioethanol production, incorporating membrane selection, membrane staging, and the conceptual design of a vacuum-refrigeration system. Their study highlights the importance of systematic membrane evaluation in optimizing process performance. Lu et al. [87] provided a comprehensive review of modeling and optimization techniques for individual pervaporation membrane modules, outlining existing challenges and future research directions in module development, including the optimization of pervaporation membrane modules. The latter was approached by Wang et al. [88], who employed computational fluid dynamics simulation for the evaluation of various flow channel designs, optimizing heat and mass transfer. While a simultaneous process, module and membrane design is likely too complex, multi-scale approaches provide a lot of potential to maximize the performance of the hybrid process. While not demonstrated for pervaporation-assisted distillation processes so far, data-driven modeling approaches may effectively enable an integrated membrane and process design, as demonstrated by Rall et al. [89,90] for ion separation membranes.

3.3. *Energy efficiency and intensified pervaporation-assisted distillation processes*

The integration of pervaporation-assisted distillation with other process intensification strategies can further foster energy savings, and improved separation efficiency, particularly for the separation of azeotropic and close-boiling mixtures. Optimization-based design methodologies have emerged as a powerful tool to systematically evaluate hybrid separation processes, considering energy efficiency, thermodynamic performance, and economic feasibility. While it is often claimed

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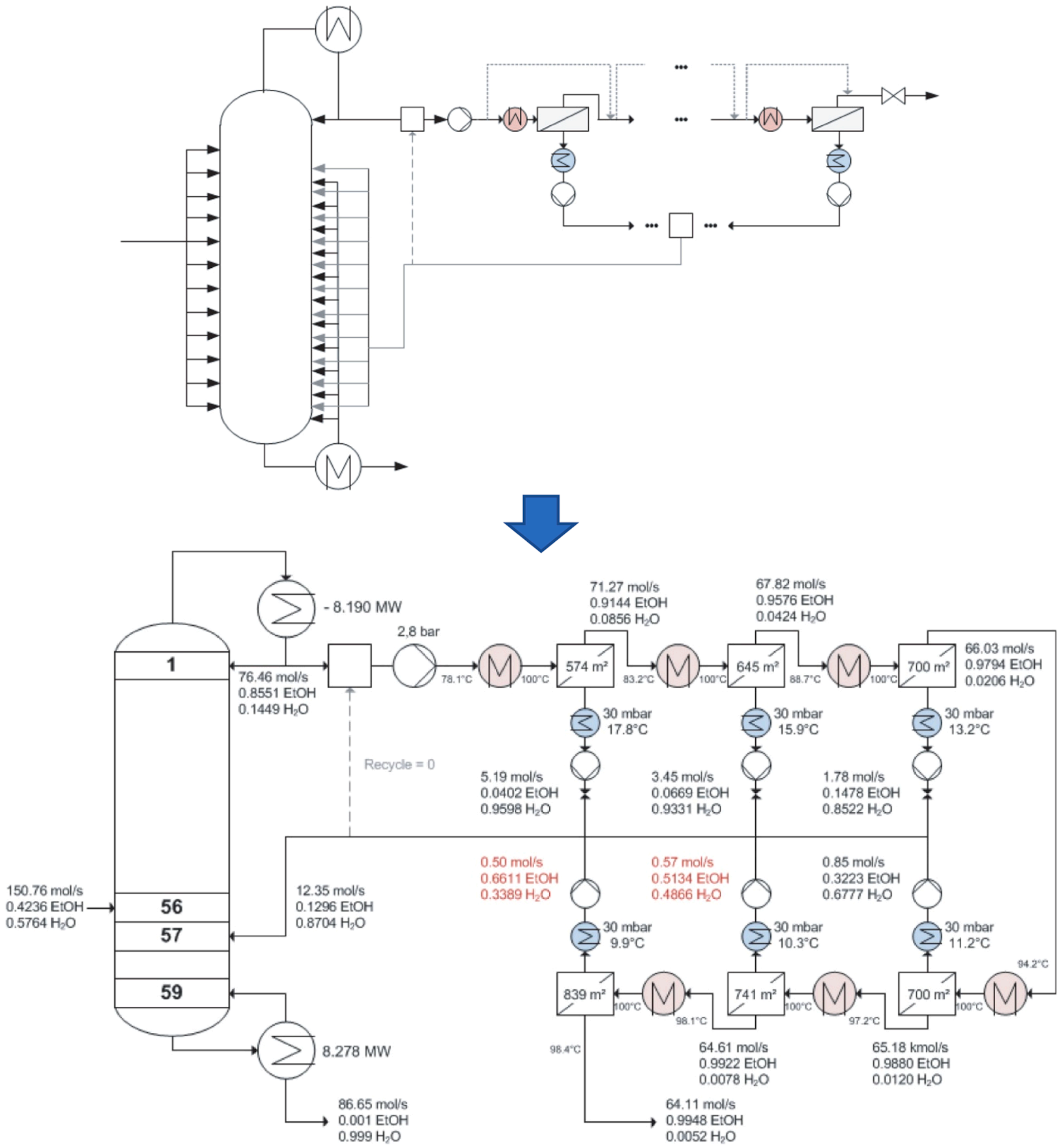

Fig. 4. Illustration of the superstructure for the pervaporation-assisted distillation process (top) and the results for the dehydration of an aqueous ethanol feed stream (bottom). Reprinted (adapted) with permission from Skiborowski et al. [76]. Copyright 2014 American Chemical Society.

that membrane processes are per se more energy efficient than distillation processes, due to a particular low efficiency of distillation in general, this is certainly not the case, as was already shown by Cussler and Dutta [91], who compared various separation processes on the basis of some idealized assumptions. More recently especially the group of Agrawal has addressed the common misconception on the efficiency and maturity of distillation processes [92,93], showcasing that distillation is not inherently inefficient and that thermodynamic efficiencies beyond 30 % are feasible by heat-pump assisted distillation columns for specific applications [94]. In a more specific analysis for the separation of different binary liquid hydrocarbon mixtures they show that under consideration of high recoveries and purities for both product streams heat pump-assisted distillation can even beat pressure-driven membrane separations in terms of energy efficiency. Based on a similar analysis Kruber et al. [9] showed that pervaporation processes are not generally more energy efficient than azeotropic distillation processes, but hybrid pervaporation-assisted distillation processes can improve the energy efficiency in case they are combined in an optimal fashion. This is illustrated for the separation of ethanol-water stream in Fig. 5 (left), indicating that the pervaporation-assisted distillation process shows a higher energy efficiency compared to a heteroazeotropic distillation process, if the top product of the distillation column does not approach the azeotropic composition. In that case the selectivity of the membrane does not need to be perfect, as indicated by the small difference of the energy efficiency of a membrane separation with a permeate stream that is pure water or has a molar composition of 90 %.Despite the potential improvement in terms of energy efficiency the condensation of the permeate remains a considerable bottleneck, as it is oftentimes performed at sub-ambient conditions in order to increase the driving force for the permeation. While this can effectively lower the required membrane area and costs, the heat of condensation actually requires work, such that the heat of evaporation for the permeating molecules strikes twice for the exergy computation of the pervaporation process.

Building on the superstructure-based optimization approach of Skiborowski et al. [76], Scharzec et al. [95] introduced a structured multi-step approach for the synthesis and intensification of

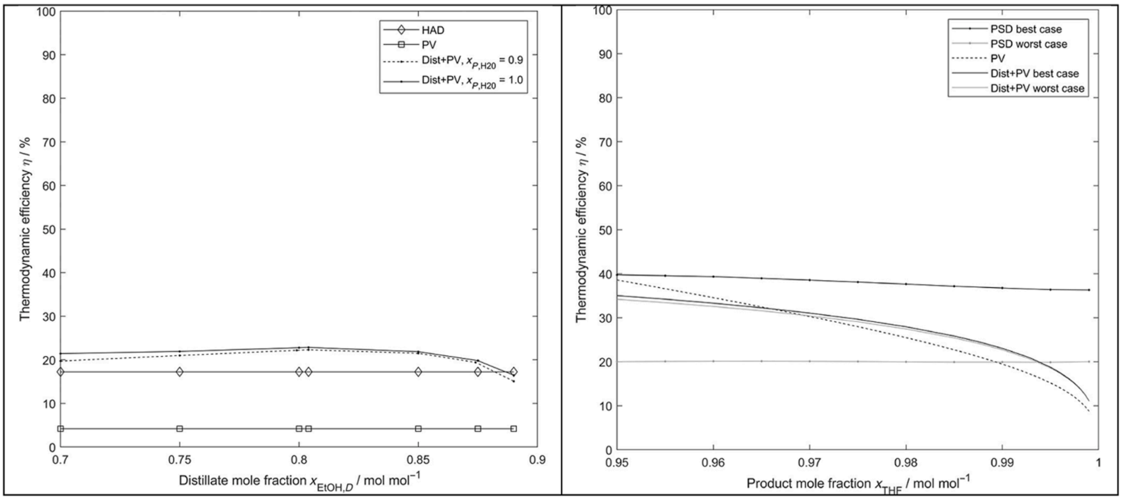

Fig. 5. Thermodynamic efficiency of a stand-alone pervaporation process (PV), a pervaporation-assisted distillation process (dist+PV) and a hetero-azeotropic distillation process (HAD) for an ethanol-water separation (left) and pressure-swing distillation (PSD) with ideal heat integration (best case) or no heat integration (worst case) for the separation of a tetrahydrofuran-water–methanol mixture (right), as presented by Kruber et al. [9].

pervaporation-assisted separation processes. The five-step framework begins with a model-based analysis of the energy-saving potential of a pervaporation-assisted distillation process, assuming the existence of an ideal membrane, comparing the process with alternative options, such as extractive or heteroazeotropic distillation. In case of a sufficient potential a techno-economic optimization is performed under consideration of a local flux model for a specific membrane, as well as possible means for energy integration, especially vapor recompression. The study demonstrates the workflow for ethanol dehydration and acetone-isopropanol-water separations. In another study Scharzec et al. [96] apply the approach for an industrial case study on the separation of a tetrahydrofuran-methanol-water mixture, for which despite an initial potential for energy savings, a pervaporation-assisted distillation processes could not compete on a techno-economical basis with a heat-integrated pressure-swing distillation process, considering experimentally determined performance models for polymeric as well as inorganic membranes. As further analyzed by Kruber et al. [9] and shown in Fig. 5 (right), the heat integrated pressure swing distillation process shows a consistently higher energy efficiency for higher product purities, while the pervaporation-assisted distillation process is superior to the pressure-swing distillation process without heat integration. Therefore, heat integration should be considered when evaluating competing process concepts. As reported by Zong et al. [97], who conducted a simulation-based study of a heat-integrated pervaporation-assisted distillation for separating an azeotropic methyl acetate and methanol azeotropes, pervaporation-assisted distillation may provide significantly lower energy requirements compared to a heat-integrated pressure swing distillation process for other separation problems. Meng et al. [98] reported energy, economic, and environmental savings of integrating pervaporation into pressure swing distillation for ethyl acetate, ethanol and water separation, concluding that the hybrid approach was superior in terms of energy efficiency and cost-effectiveness. These studies highlight the need of a systematic process optimization of competitive process concepts to evaluate the true potential of pervaporation-assisted distillation processes. Chia and Sorensen [85] presented a refined superstructure model for hybrid pervaporation-assisted distillation processes with a variable number of membrane stages, showcasing the economic potential of the hybrid process in comparison with an extractive distillation process for a wide range of ethanol-water feed conditions. In a subsequent work, Chia et al. [99] explored single- and multi-objective optimization for pervaporation-assisted distillation processes, including a combination with dividing wall column (DWC), leveraging a combination of metaheuristic algorithms and gPROMS. The results did however indicate that the more complex, intensified process design with a DWC is economically not superior to a configuration with two distillation columns and an intermediate membrane separation. Do Thi et al. [100] further evaluated the combination of hydrophilic and organophilic membranes for pervaporation-assisted distillation for alcohol-water separations, concluding that hybrid processes with hydrophilic membranes were more effective.

Beyond steady-state optimization, some reaserchers have also recently explored the possibility of an enhance separation performance by dynamic operation. Atehortua et al. [101] recently explored the concept of dynamic pervaporation for ethanol separation, demonstrating that periodic operation may increase flux by up to a factor of ten. This explorative study indicates a huge potential of operational adjustments, but needs further validation, especially considering long term stability, transferability and integrated operation. After all, even the characterization of membrane performance is usually performed at quasi stationary operating conditions for a longer period in time to get consistent measurements [102]. Consequently, also the derivation of dynamic models and respective experimental validation are needed for such investigations, considering that especially the separation performance of polymeric membranes will react on changing operating conditions with different time constants.

3.4. Pervaporation-assisted extractive distillation processes

Several studies have evaluated extractive distillation and pervaporation-assisted distillation as competitive process concepts [76, 85]. Genduso et al. [103] even explored the potential use of high-flux membranes that do not necessarily provide high separation factors in order to convert an extractive distillation sequence into a pervaporation-assisted distillation processes. The retrofitting concept, which is illustrated in Fig. 6 was reported to save up to 38 % of the overall energy requirements of the extractive distillation process.

Prior to the last decade only the work of Koczka et al. [22] has considered the combination of both as pervaporation-assisted extractive distillation. The authors did investigate the use of PERVAP® 2210 membranes in the scope of a THF recovery from a mixed stream with water and methanol, reporting that a pervaporation-assisted extractive distillation process with water as solvent effectively reduces the THF losses and the utility cost compared to the considered benchmark processes. In the recent decade pervaporation-assisted extractive distillation has received a considerable increase in interest with various

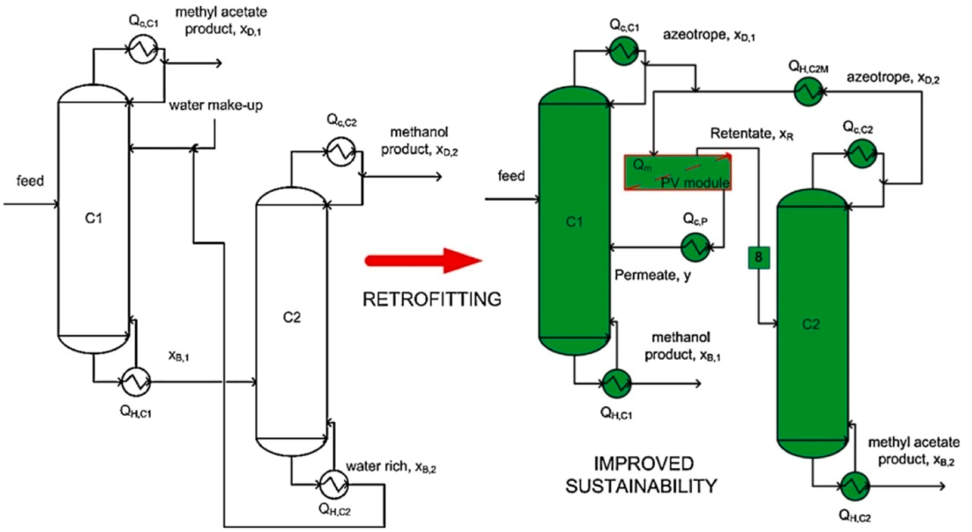

Fig. 6. Illustration of potential retrofit of an extractive distillation process to a pervaporation-assisted distillation process. Reprinted from [103], with permission from Elsevier.

publications on the conceptual design, primarily from Chinese research groups. The work of Novita et al. [104] is an early exception. The authors proposed a conceptual design for a pervaporation-assisted extractive distillation process for the dehydration of ethanol, isopropanol, and tert-butyl alcohol using the well-established solvent ethylene glycol as an entrainer. Based on flowsheet simulations with Aspen Plus they projected up to 20 % cost savings and energy reductions ranging from 8 % to 41 % depending on the specific alcohol.

Dai et al. [105] assessed the purification of diisopropyl ether and isopropyl alcohol with pervaporation-assisted extractive distillation, reporting 10–20 % of economic savings and an a 8 % reduction in global warming potential compared to conventional extractive distillation. Meng et al. [98] analyzed the separation of a mixed stream of ethyl acetate, ethanol, and water, with a pervaporation-assisted extractive distillation process, in which the pervaporation membrane is responsible for the separation of water, while concentrating the entrainer for the extractive distillation process. The respective process configuration is depicted in Fig. 7. By comparing the pervaporation-assisted extractive distillation process with a thermally coupled and a heat-integrated extractive and pressure swing distillation processes, the authors conclude that the pervaporation-assisted extractive distillation process provides the lowest heat requirements and competitive economics with the slightly more economic thermally coupled extractive distillation process. However, the pervaporation-assisted extractive distillation process shows the lowest energy efficiency of all considered options, which is due to the sub-ambient condensation of the permeate stream, which unlike all other condensers in the distillation processes actually requires work. In a similar study Zhu et al. [106] did investigate the same process configuration for the separation of a ternary azeotropic mixture of acetone, isopropanol, and water. They performed a techno economic optimization of the process by means of a simulation-based iterative optimization. By comparison with a basic extractive distillation process and a life cycle assessment they conclude that the pervaporation-assisted distillation process provides better economic and environmental performance even in case of an extractive distillation with an additional heat pump for energy integration. Further

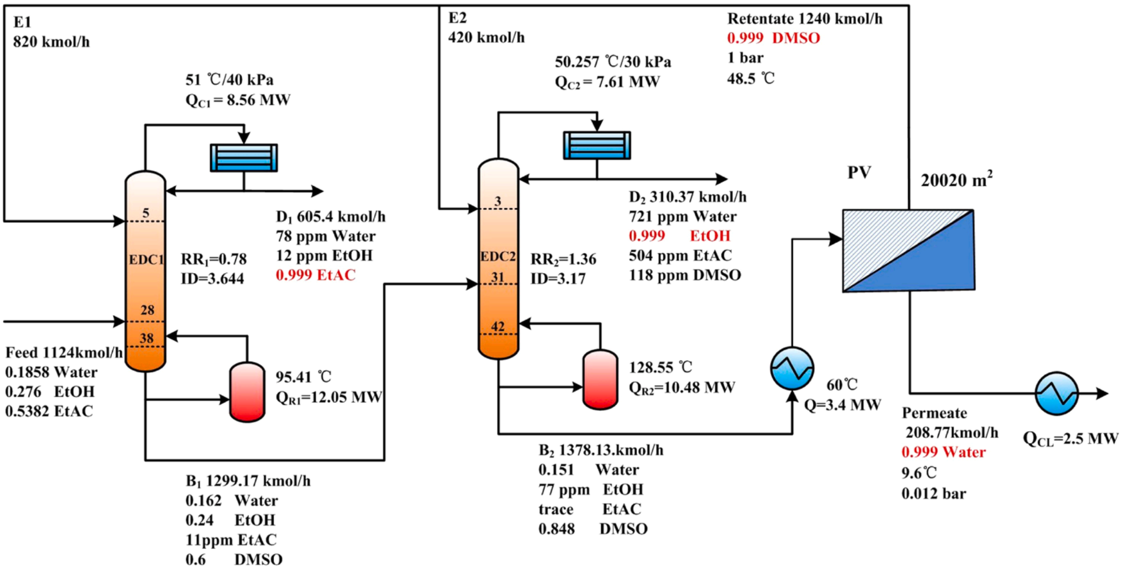

Fig. 7. Illustration of pervaporation-assisted extractive distillation process for the separation of a mixed stream of ethyl acetate, ethanol, and water with DMSO as solvent. Reprinted from [98], with permission from Elsevier.

advancements were made by Wang et al. [107], who also applied techno-economic and environmental analysis to optimize a pervaporation-assisted extractive distillation process for the separation of a mixture of acetonitrile, water, and n-propanol. They showed a superior economic and environmental performance of the pervaporation-assisted hybrid process compared to an extractive distillation process, both including mechanical vapor recompression for heat integration. All these studies have in common that a hydrophilic membrane is used for the final recovery of water and the concentration of the heavy boiling solvent.

Given the complexity of the process design problems and the possibilities offered by metaheuristics for simulation-based optimization, recent research activities have further focused on multi-objective optimization (MOO) to improve sustainability and efficiency of the pervaporation-assisted extractive distillation. Zhang et al. [108] utilized MOO for pervaporation-assisted extractive distillation processes for the separation of a mixture of cyclohexane, isopropanol, and water. There comparison considered a basic extractive distillation process, as well as a thermally-coupled extractive distillation process in a equipment-integrated dividing wall column and found the pervaporation-assisted extractive distillation process to require less energy, have lower CO_2 emissions and cost saving. Yet, it needs to be noted that the dividing wall column did primarily provide cost savings in terms of investment costs, as the possible energy savings are quite small, as is reported for other cases of extractive distillation in several literature studies [109]. In another study Zhang et al. [110] apply MOO for the optimization of a pervaporation-assisted extractive distillation process for the separation of a mixture of tetrahydrofuran, toluene, and water, considering again the same process configuration depicted in Fig. 7. Their comparative evaluation with a basic extractive distillation process, in which the water needs to be separated from the heavy boiling solvent in a distillation column as top product, shows superior economic, energetic, and environmental performance compared to conventional extractive distillation for a variety of feed compositions. Another MOO study by Jiao et al. [110,111] also performed a comprehensive economic, environmental, energy, and exergy analysis of several basic, thermally-coupled and heat integrated extractive and extractive pressure-swing distillation processes with the pervaporation-assisted distillation process configuration depicted in Fig. 7, for the separation of a mixture of ETBE, ethanol and water. Unlike the other authors for other separation problems, they do find the heat-integrated extractive distillation process to be competitive with the pervaporation-assisted distillation process in all of the categories. Yet, both are considerably outperforming the basic and thermally-coupled process configurations. Note, that the pervaporation process in this work at least appears to operate at a permeate pressure that enables condensation with cooling water. In another work Li et al. [112] extended this work by optimizing the separation of a mixture of acetonitrile, ethanol, and water using pressure variation and pervaporation, demonstrating 15 % cost savings and 20 % emission reductions compared to conventional extractive distillation.

While all the above publications evaluated the separation of ternary mixtures with a similar topology, considering the pervaporation-assisted extractive distillation configuration depicted in Fig. 7, Xu et al. [113] examined the separation of a multi-azeotropic mixture consisting of diisopropyl ether, isopropyl alcohol, and water, concluding that pervaporation-assisted extractive distillation with ethylene glycol is a viable solution in terms of total annual cost, energy consumption, and environmental impact. Yet, the authors do not provide a comparative assessment with alternative process concepts that operate without pervaporation.

In summary, there has been a significant increase in conceptual studies on the potential of pervaporation-assisted extractive distillation processes, showcasing that the hybrid configurations can outperform extractive and extractive pressure-swing distillation processes even under consideration of additional means for energy integration, such as heat integration and thermal coupling. However, most of these studies have investigated the separation of ternary mixtures with a similar topology for which the final separation of water and a heavy boiling entrainer is performed by means of a hydrophilic pervaporation membrane, as depicted in Fig. 7. Other, especially more complex separation problems have not yet been investigated, leaving considerable room for improvement in the context of industrial applications.

3.5. *Pervaporation-assisted reactive distillation processes*

Unlike pervaporation-assisted extractive distillation, pervaporation-assisted reactive distillation has already been investigated in the 1990, e.g. for the production of carboxylic acids [114] and Ethyl tert-butyl ether [115]. An overview on pervaporation and vapor-permeation-assisted reactive distillation and some more detailed examples are provided in the book chapter of Holtbrügge and Pela [116], which also provides an overview on different reaction systems that have been investigated in different studies. These include the synthesis of ethyl acetate, n-propyl propionate, fatty acid i-propyl ester, trimethyl borate, tert-amyl ethyl ether, n butyl acetate and dimethyl carbonate and propylene glycol. Over the past decade, various simulation-based studies have explored the feasibility and benefits of pervaporation-assisted reactive distillation across multiple chemical processes. Lee et al. [117] assessed a pervaporation-assisted reactive distillation process for ethyl acetate synthesis via transesterification, demonstrating that the hybrid process is economically competitive when membrane costs are sufficiently low, with a break-even cost of 270 $/m^2. Norkobilov et al. [118] compared conventional reactive and pervaporation-assisted reactive distillation for ethyl tert-butyl ether production, concluding that the hybrid process enables savings of up to 50 % in utility requirements. Sun et al. [119] performed a conceptual design study for the synthesis of glycerol carbonate by transesterification of dimethyl carbonate, evaluating a pervaporation-assisted and a pressure swing reactive distillation process. Their results showed performance improvements of about 20 % in terms of process economics and 30 % in terms of environmental impact criteria. Liu et al. [120] developed a novel process concept based on the integration of a side-reactor distillation column with pervaporation membranes for the synthesis of n-propyl propionate via esterification of n-propanol with propionic acid. The process concept, which is illustrated in Fig. 8, is particularly interesting for reactions that require larger residence times and the results indicate that the integration of the pervaporation membranes enables energy savings of about 18 %, demonstrating the potential for further process intensification.

Recent efforts have focused on optimization-based approaches and further process intensification to maximize the benefits of pervaporation-assisted reactive distillation. Harvianto et al. [121,122] performed a conceptual design optimization of a reactive distillation system with high-selectivity pervaporation membranes for butyl acetate production, effectively separating a methanol-methyl acetate azeotrope in the recycle stream. They further improve the energy and cost efficiency of the hybrid process by including thermal coupling via a side stripper. This concept is illustrated in Fig. 9. Babaie and Esfahany [123] conducted a comparative simulation-based optimization of twelve process configurations, incorporating pervaporation and heat integration into reactive distillation for tert-amyl methyl ether production. The results indicate distinct advantages over extractive and pressure swing reactive distillation. Particularly a heat-integrated reactive distillation column with feed splitting in combination with pervaporation supposedly was capable to reduce the energy demand and cost by >40 % compared to a non-integrated pervaporation-assisted or pressure-swing reactive distillation process. In their subsequent study, Babaie and Esfahany [124] again evaluated twelve process configurations for the production of ethyl tert-butyl ether, for which especially combinations of thermally-coupled reactive distillation in dividing wall columns in combination with pervaporation were investigated. The study identified a hybrid pervaporation-assisted reactive dividing wall column as the

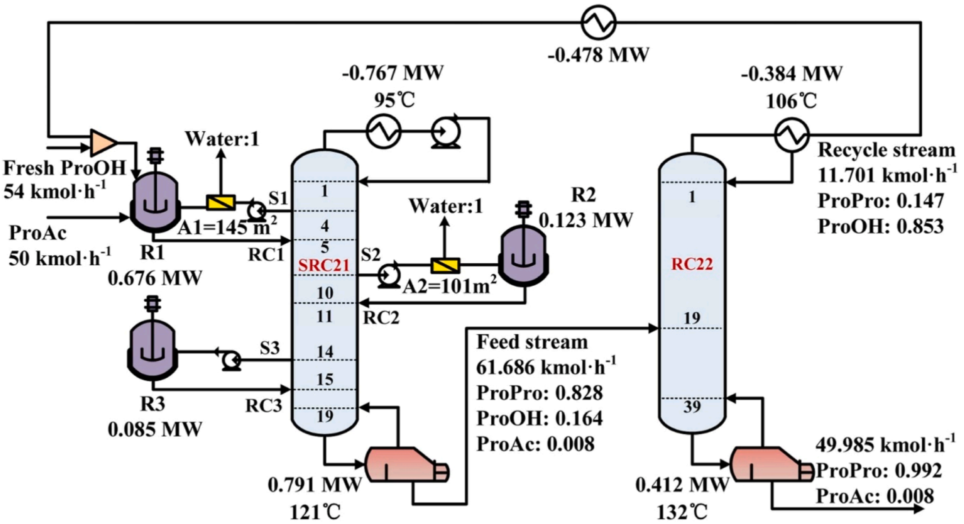

Fig. 8. Integration of a side reactor distillation with pervaporation membranes to enable sufficiently large residence times for an esterification reaction for the synthesis of n-propyl propionate via esterification of n-propanol with propionic acid. Reprinted from [120], with permission from Elsevier.

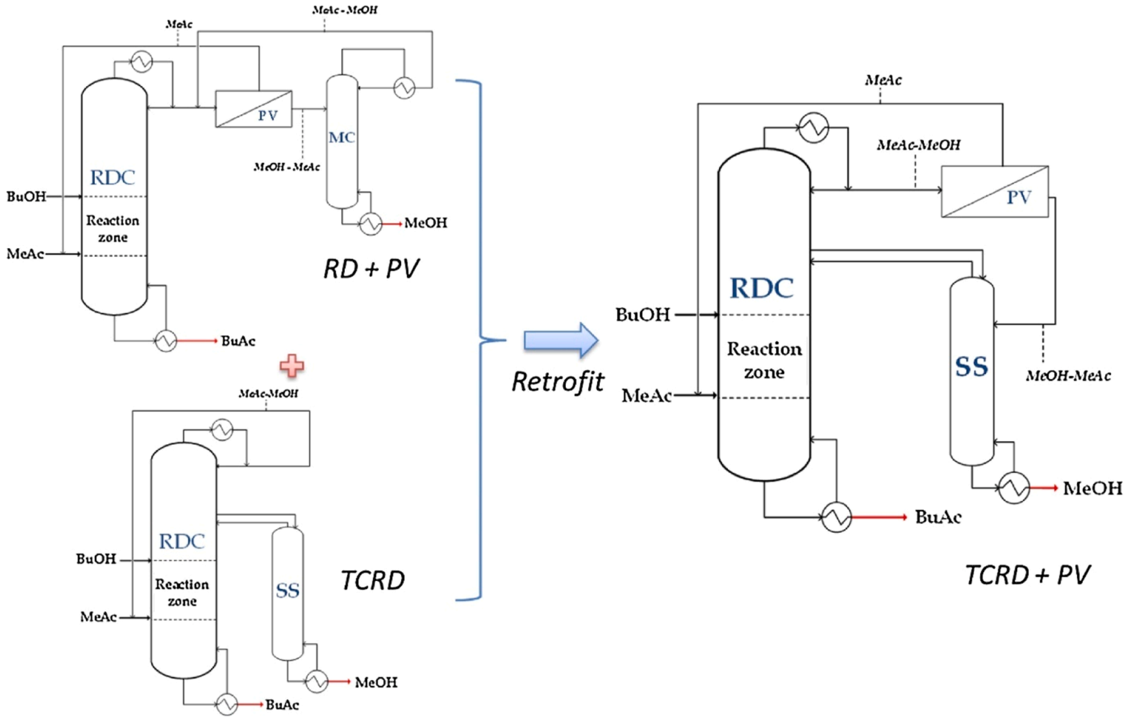

Fig. 9. Integration of reactive distillation with thermal coupling and pervaporation to a thermally coupled pervaporation-assisted reactive distillation process for the synthesis of butyl acetate. Reprinted from [122], with permission from Elsevier.

most energy- and cost-efficient process, with cost savings of >50 % compared to the conventional process with separate reactors and distillation columns and 30 % compared to a reactive dividing wall column.

Further process intensification strategies were explored by Li and Kiss [125], who developed a novel pervaporation-assisted pressure swing reactive distillation process for dimethyl carbonate production. Their simulation-based study evaluated an improvement potential of 30 % energy savings and 40 % cost reduction compared to a conventional reactive distillation process. Similarly, Zhao et al. [126] conducted a process design study for the transesterification of methyl acetate and butanol to produce n-butyl acetate. They compared the performance of a pervaporation-assisted reactive distillation with an extractive reactive distillation and a side-line extractive reactive distillation process, showing somewhat lower energy requirements and cost for the pervaporation-assisted reactive distillation. Yet, these savings were evaluated to be considerably lower than in other studies, with <10 % in terms of energy demand and <2 % in terms of process economics. Duanmu et al. [127] are the first to conduct a superstructure-based optimization of pervaporation-assisted reactive dividing wall columns as well as alternative pressure swing reactive distillation, building on the model development from the work of Chia et al. [99] and a combined particle swarm optimization and outer approximation approach for optimization [128]. Their study reports up to 24 % energy savings for the pervaporation-assisted reactive distillation process compared to pressure swing reactive distillation. While the considered case study resembles an esterification reaction for ethyl acetate production it is considered as an abstract reaction system for an equilibrium limited reaction.

In order to support the development of advanced reactive distillation processes, including pervaporation-assisted reactive distillation, Pazmino-Mayorga et al. [129] proposed a systematic method that builds on the analysis of basic thermodynamic and kinetic properties, applying first principles and heuristics. The aforementioned optimization-based synthesis approach of Kuhlmann et al. [81] in principle also enables a model-driven synthesis of membrane-assisted reactive distillation processes, which was illustrated for a vapor permeation-assisted reactive distillation for the transesterification of propylene carbonate with methanol [82]. Yet most studies in literature build on expert knowledge for process synthesis and the orientation on similar problems.

Overall, it can be concluded that pervaporation-assisted reactive distillation has shown considerable performance improvements in a variety of conceptual design studies, proofing to be a valuable strategy for process intensification, delivering enhanced reaction conversions, lower energy consumption, and improved sustainability. Most of the existing studies focus on esterification and transesterification reactions. Recent studies have provided strong evidence for the economic viability and environmental benefits of the pervaporation-assisted reactive distillation processes in comparison to alternative process concepts. While simulation-based investigations dominate current research, further experimental validation and industrial-scale implementations will be essential to unlock the full potential of this hybrid separation technology.

3.6. *Pervaporation-assisted distillation processes with experimental investigations*

While the literature is quite rich in publications on experimental investigations of specially synthesized pervaporation membranes in lab-scale experiments as well as conceptual design studies on pervaporation and pervaporation-assisted distillation processes, there are only few publications that actually report on experimental investigations of commercial pervaporation membranes in pervaporation-assisted distillation processes, or at least a dedicated experimental investigation in the context of a conceptual design study. These studies are however of significant importance in advancing the practical implementation and performance of pervaporation-assisted distillation processes.

Rom et al. [130] explored the integration of pervaporation with distillation for butanol purification, demonstrating that pervaporation can effectively extract butanol from fermentation broths before further purification via heteroazeotropic distillation. While pervaporation is rather used as a preconcentration prior to heteroazeotropic distillation than a hybrid process, the results provide experimental confirmation of the energy-saving potential of pervaporation-assisted processes in biofuel production. Following the previously described multistep approach (cf. Section 3.3), Scharzec et al. [96] conducted an experimental screening of polymeric and inorganic membranes for the purification of tetrahydrofuran (THF) from methanol-water mixtures. Their study combined laboratory-scale pervaporation experiments with an optimization-based design for pervaporation-assisted distillation.

Publications on pilot-scale investigations are even more scarce. When evaluating the performance of pervaporation-assisted processes on the basis of models developed from laboratory experiments it is important to note that non-idealities in technical modules cannot be ruled out and that driving force limiting effects, such as concentration polarization can cause considerable drops in module efficiency [13]. Matuschewski et al. [131] and Schiffmann and Repke [59] report on the experimental investigations and modeling of the separation performance of organophilic pervaporation membranes in a specially constructed pocket module. The studies include a comparison of the measurements in a lab-scale test cell with an active area of 49 cm^2 and the pilot-scale module with an active area of 0.63m^2, representing a scale up of the membrane area by a factor >100 and the non-ideality of the technical module. Kujawska et al. [132] performed investigations on a SULZER ECO-001 pilot plant for ethanol dehydration with hydrophilic composite PERVAP™ poly(vinyl alcohol) PVA membranes with plate and frame modules containing membranes with an active area of about 1.5 m^2. In one of the most recent studies Baik et al. [133] provide pilot-scale experiments for the azeotropic purification of dimethyl carbonate (DMC), considering a special heat-exchanger module with HybSi® membranes (0.7m^2 surface area) are evaluated experimentally, while a model-based assessment compares the pervaporation-assisted distillation process with a pressure-swing distillation process. Nishiyama et al. [134] present an extensive study of specially synthesized PDMS-ZSM-5 membranes for the dehydration of isopropanol, presenting the results of lab-scale measurements of small stamps of about 43cm^2, as well as pilot-scale experiments with different arrangements of connected pressure vessels holding up to 20 spiral-wound elements, each providing an active membrane area of 0.47m^2, adding up to almost 10m^2.

Despite these large pilot-scale investigations on pervaporation membranes even less data on the experimental investigation of integrated hybrid pervaporation-assisted distillation processes is available. Holtbrügge et al. [135,136] conducted one of the few pilot-scale experimental studies on integrated membrane-assisted distillation, which does however include vapor-permeation instead of pervaporation in combination with a reactive distillation column for the synthesis of dimethyl carbonate (DMC) and propylene glycol. Their work demonstrates the ability of membrane integration to shift reaction equilibria and enhance product purity. The study remains a key reference for the experimental application of membrane-assisted separation in reactive distillation. Given the lack of experimental validation of the integrated hybrid plants, future research should build upon the theoretical findings and further expand experimental validation of theoretically proficient hybrid processes, demonstrating the operability and performance of the integrated pervaporation-assisted processes, in order to enable a broader industrial adoption of pervaporation-assisted distillation processes.

3.7. *Pervaporation-assisted distillation in a single unit operation*

Distillation-pervaporation in a single unit (DPSU) was developed as an additional process intensification step for pervaporation-assisted distillation that integrates pervaporation membranes directly within a distillation column [52]. This novel approach enhances mass transfer efficiency, reduces energy consumption, and enables the separation of azeotropic and close-boiling mixtures beyond distillation boundaries in a single integrated piece of equipment. Nevertheless, similar to the integration of reaction and separation, the applicability of such an integrated unit operation mandates a sufficiently large overlap of the individual operating windows [137]. The DPSU concept has received significant attention in the recent decade and major advances were made for modeling, design and experimental demonstration, as well as potential extension to more complex applications, including reactive distillation.

The DPSU concept was first introduced by Fontalvo and Keurentjes [52] as an equipment-integrated hybrid distillation–pervaporation system designed to overcome distillation boundaries in multicomponent mixtures. The initial study presented a rate-based simulation approach that incorporated an intermediate packed bed of semi-permeable membranes within the distillation column, as illustrated in Fig. 10. The results showcased the general feasibility of the DPSU configuration and the potential to enhance separation efficiency for the separation of two ternary mixtures, consisting of MTBE, methanol and 1-butane, as well as ethanol, ethyl acetate and water.

Further development of the DPSU concept focused on systematic design methodologies, particularly using residue curve maps (RCMs). León and Fontalvo [139] analyzed RCM of different systems to identify potential applications of DPSU and establish general design principles for the integrated column. Subsequently, León and Fontalvo [140]

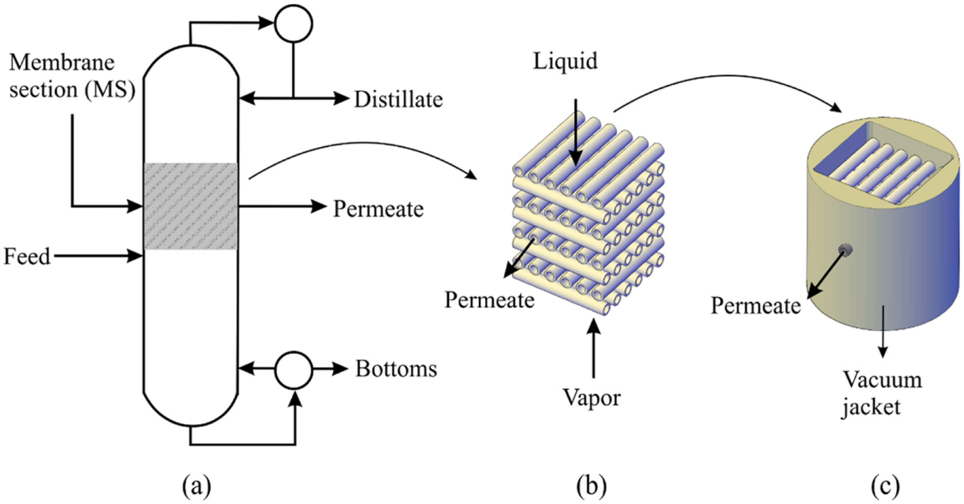

Fig. 10. General scheme of the Distillation-Pervaporation in a Single Unit (DPSU). Reprinted with permission from [138]. Copyright 2020 American Chemical Society.

proposed a short-cut design method based on RCMs, illustrating that DPSU columns can achieve feasible separations even when product compositions are separated by distillation boundaries, while thermodynamic limitations pertain if the azeotropes generate isovolatility lines, producing different separation paths for a specified membrane selectivity. The application of the short-cut design approach is illustrated for four ternary mixtures representing different topological classifications according to Serafimovs classification [141]. The different tools developed for the design and analysis of the DPSU were furthermore summarized by León and Fontalvo [139].

Another major advancement constitutes the experimental validation of the DPSU concept. The first experimental evaluation of a DPSU column by León, Schuur, and Fontalvo [142], who demonstrated the separation of an ethanol-isopropanol-water azeotropic mixture using a silica membrane selective to water in a batch operation. This study provided the first empirical proof of the DPSU concept, confirming its viability for azeotropic mixture separation. Further experimental investigations in a laboratory set-up with conventional packed and membrane packed sections were presented by León and Fontalvo [138], using specially produced inorganic membranes, produced by dip-coating several silica layers on the external γ-Al_2O_3 layer on top of commercial α-Al_2O_3 tubes (Hyflux, Singapore). For the membrane section, a silica (hydrophilic) membrane module with 19 layers of membrane tubes in a cross-in-line arrangement was used. By selectively removing water through the silica membranes in a DPSU column, the internal compositions in the distillation column were shifted to low water compositions, and the distillation boundary was effectively overcome by the DPSU columns, showcasing the huge potential of this process intensification technology. While the DPSU has various benefits and the potential to significantly reduce the number of unit operations, it is however important to keep in mind the necessity of overlapping operating windows.

The potential of DPSU for hydrocarbon separation was further explored by Xu et al. [143], who applied shortcut methods and Aspen simulations to evaluate its feasibility for olefin/paraffin (ethylene/-ethane) separations, highlighting the possible advantages of DPSU in improving separation efficiency in petrochemical applications. Additionally, Fu et al. [144] investigated the recovery and purification of propylene glycol monomethyl ether (PM) within the DPSU concept with a conceptual study as well as lab-scale experiments. The conceptual study indicated that DPSU could enhance the economic benefits of the hydrogen peroxide to propylene oxide (HPPO) process, making it a viable solution for epichlorohydrin production.

Expanding beyond conventional separations, Han et al. [145] introduced the inter-integrated reactive distillation with vapor permeation (R-VP-D) process, which integrates reaction, vapor permeation, and distillation into a single unit, building on the DPSU concept. This approach was validated through pilot-scale experiments, marking a significant step in process intensification. Finally, Liu, Li, and Gao [146] extended the DPSU concept further by integrating vapor permeation into reactive distillation. Using Aspen Custom Modeler (ACM) and Aspen Plus for conceptual studies. They developed a two-dimensional VP module and verified its accuracy with experimental results, demonstrating its potential for efficient 1,3-dioxolane production. While the latter studies transferred from pervaporation to vapor permeation, the phase contact with the membrane in the distillation column is likely mixed, with both vapor and liquid.

While the DPSU concept has shown promise in various applications, several challenges remain and performance evaluations should consider a direct comparison with an externally integrated hybrid PV-assisted distillation process that can exploit separate operating windows for each unit operation. Future research should provide such comparative evaluations focus on optimizing membrane materials for higher selectivity and durability, improving process integration strategies for energy efficiency, and expanding experimental validation to industrial-scale applications. The combination of advanced modeling tools and experimental studies will be crucial in further establishing DPSU as a standard technique in process intensification. The DPSU process represents a significant innovation in hybrid separation technologies, enabling efficient separations beyond traditional distillation limits. Through continuous advancements in modeling, design methodologies, and experimental validation, DPSU has evolved into a versatile and energy-efficient alternative for complex separations. As research progresses, its integration into large-scale industrial applications will further solidify its role in sustainable and intensified separation processes.

4. Summary and conclusion

The current review provides an overview of the most recent developments in the research on pervaporation-assisted distillation processes. Overall, it can be concluded that various promising process concepts and especially advanced energy-integrated process concepts have been proposed for PV-assisted distillation, showcasing the competitiveness and potential superiority of the membrane-assisted distillation processes compared to other intensified azeotropic distillation processes. A large number of conceptual design studies has illustrated the potential benefits that pervaporation-assisted distillation process can provide when properly designed. Optimization-based tools have enabled the design of complex configurations with multiple distillation columns, pervaporation stages and different means for energy integration. As envisioned by van der Bruggen and Luis [44] these systems engineering tools can help to pave the way to a broader industrial application pervaporation-assisted distillation processes. They can also enable a targeted development of organophilic membranes, by steering the requirements in terms of stability and separation performance for specific applications, evaluating the integrated process configurations. The study on the separation of an acetone, isopropanol, water mixture by Scharzec et al. [95] does e.g. evaluate the potential of an organophilic membrane for the separation of isopropanol, assuming a the availability of a membrane with a moderate separation performance. Overall, the availability of suitable membranes with a sufficient separation performance and long-standing stability will remain a fundamental requirement for the development of hybrid processes for specific applications. Yet, hybrid processes may enable beneficial conditions for membrane application, focusing on a small operating window. In order to further advance the development of PV-assisted distillation processes research in the following areas should be promoted to overcome remaining challenges towards industrial applications:

- Predictive Modeling for Pervaporation separations

While distillation columns are easily evaluated in commercial process simulators on the basis of equilibrium-stage models that exploit the availability of predictive thermodynamic models, pervaporation lacks both, the availability of models for membrane modules in commercial process simulators, as well as the availability of predictive models that enable an application of the separation performance for a specific separation problem. To this end the collective development of large experimental databases and data-driven or hybrid models for flux and selectivity predictions provide huge potential. This calls for a collaboration between researchers, membrane manufacturers and potential end users.

- Process Optimization Tools

The effective integration of pervaporation membranes and distillation columns requires tailored operating conditions to maximize the synergies and leverage available energy sources. Superstructure models and rigorous optimization methods effectively enable a simultaneous consideration of the multitude of concurrent design decisions, especially in the context of multi objective optimization. While different of such approaches have been demonstrated to be effective in research publications, their utilization needs to be advanced to industrial applications, requiring collaborations between researchers, software companies and industrial end users.

- Consideration of additional means for process intensification

While pervaporation-assisted distillation as a hybrid separation process can be considered as a concept for process intensification it is important to evaluate these process concept in conjunction with energy integration strategies, such as heat integration, thermal coupling, and heat pump applications, in order to maximize energy efficiency and conduct a fair techno-economic comparisons between pervaporation-assisted and alternative distillation processes, which may provide a bigger potential for energy integration. Recent studies just started to conduct such studies, e.g., for pervaporation-assisted extractive distillation processes, as described in Section 3.4. Yet, as highlighted before, so far, most studies have focused on comparable process configurations as thus similar separation problems. Future research should enable more standardized evaluations of competitive process options with means for energy integration, mandating advanced optimization tools and flexible modeling tools. Furthermore, the investigation of dynamic operation strategies and their potential to intensify pervaporation-assisted distillation systems may be of interest.

- Life Cycle Assessment and multi-criteria evaluation

While most conceptual design studies consider some form of energy and techno-economic-based assessment or optimization of the pervaporation-assisted processes, further socio-environmental metrics are rarely considered and if so, mostly in terms of greenhouse gas emissions that directly correlated with energy consumption. Especially the limited lifespan of membranes, which is usually considered in terms of repetitive membrane replacement costs, necessitates an assessment of their environmental impact, particularly regarding end-of-life treatment and disposal. So far the work of Do et al. [147] seems to be the only one that studies environmental and socio-economic effects of different separation processes consisting of pervaporation and distillation with a multi-criteria assessment. Yet, membrane replacement is considered only in terms of economics in this work. PV-assisted processes should consequently be evaluated in comparison to other separation processes on the basis of energy, exergy and techno-economics, further complemented by a socio-environmental assessment in the future.

- Experimental Validation of advanced process concepts

While the performance of individual membranes is frequently evaluated experimentally, lab-scale experiments are oftentimes conducted at inappropriate conditions, especially applying high vacuum conditions with very low permeate pressure to increase the driving force for mass transfer, while applying freeze traps with liquid nitrogen [102,148]. These concepts translate however quite badly to industrial applications for which the economic burden of expensive cooling brine or the need for sub-ambient heat pumps necessitates a tradeoff between a decrease in driving force with larger membrane area requirements and extensive cooling costs. While as outlined in Section 3.6 at least some studies on the performance of membrane modules exist, experimental investigations of the hybrid pervaporation-assisted distillation configurations are extremely scarce. Due to the need for sufficient column heights, pilot-scale demonstrations would be required to validate the reliability and advantages of pervaporation-assisted distillation. These investigations mandate the collaboration between researchers, membrane provides, as well as engineering companies and end users. To this end, there is probably an excess in industrial knowledge that is not openly available.

CRediT authorship contribution statement

Maria Polyakova: Writing – original draft, Visualization. **Mirko Skiborowski:** Writing – review & editing, Writing – original draft, Project administration, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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