



Process intensification by integration of distillation and vapor permeation or pervaporation - An academic and industrial perspective

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ARTICLE INFO

Keywords:

Process intensification
Membrane
Distillation
Vapor permeation
Pervaporation

ABSTRACT

Since membrane separations, such as vapor permeation (VP) or pervaporation (PV), are not limited by vapor-liquid equilibrium, their coupling with distillation can exert a synergistic effect, overcome the thermodynamic limits of distillation, and improve energy efficiency, especially suitable for the separation of azeotropic mixtures that otherwise requires special distillation processes. Therefore, there is an increasing number of such studies, and it is of great significance to comprehensively explore the process integration of distillation with VP or PV. This review first introduces the mechanism model of membrane separation and membrane materials, then comprehensively summarizes the academic research in terms of hybrid configurations of distillation with VP or PV in the following aspects: separation of azeotropic or close-boiling mixtures, promoting reactions by selectively removing a product, and energy savings, providing guidelines for subsequent application and future research. Finally, this review gives typical industrial cases of distillation and membrane-coupled separation processes and highlights some deficiencies of current research in this area.

1. Introduction

Thermal separation processes, such as distillation, drying, and evaporation, are known to be energy-intensive and usually account for 30–80% of the energy used in the production of bulk and specialty chemicals [1]. For the U.S., with more than 40,000 distillation columns in operation [2], the estimated share of these thermal separation processes of the country's total energy consumption is estimated to add up to about 12% [3]. With the increasing awareness of human ecological and environmental protection and the decreasing reserves of non-renewable fossil energy, the energy-intensive chemical industry has encountered unprecedented challenges that increased the interest in reducing energy consumption and improving energy efficiency. Faced with these challenges, the 100th Anniversary of Industrial & Engineering Chemistry Research [4] proposed that process intensification (PI) is one of the most promising development paths for the chemical industry, with the maximization of synergistic effects in integrated processes as one potential means for PI, providing guidance for researchers and process engineers.

Process integration provides huge potential for improvements for energy-intensive separation operations in the chemical industry. It can be accomplished by combining the same unit operation type, such as, e.g., thermal coupling of distillation columns and the equipment-integrated dividing wall column, or different types of unit operations [5]. The latter, the integration of unit operations based on different separation mechanisms, results in so-called hybrid separation processes that provide synergistic effects, which may improve energy efficiency and overcome the thermodynamic limitations of independent operations [6]. One of the best-known examples of hybrid separation processes is the combination of distillation and membrane separation.

Membrane separation as a unit operation refers to the separation, classification, purification, or enrichment of two-component or multi-component systems using natural or synthetic membranes with selective permeation ability, driven by external energy or chemical potential difference [7–10]. While pressure-driven membrane separations, such as ultrafiltration, nanofiltration, and reverse osmosis provide a significant potential for energy-efficient and gentle separation processes, the current review paper focuses on vapor permeation (VP) and pervaporation

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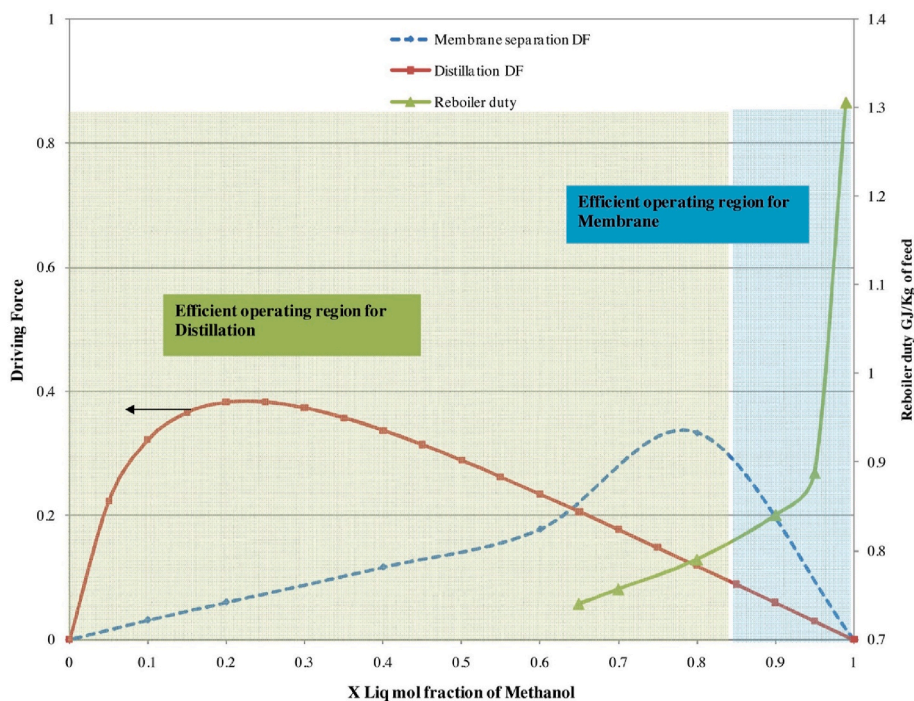
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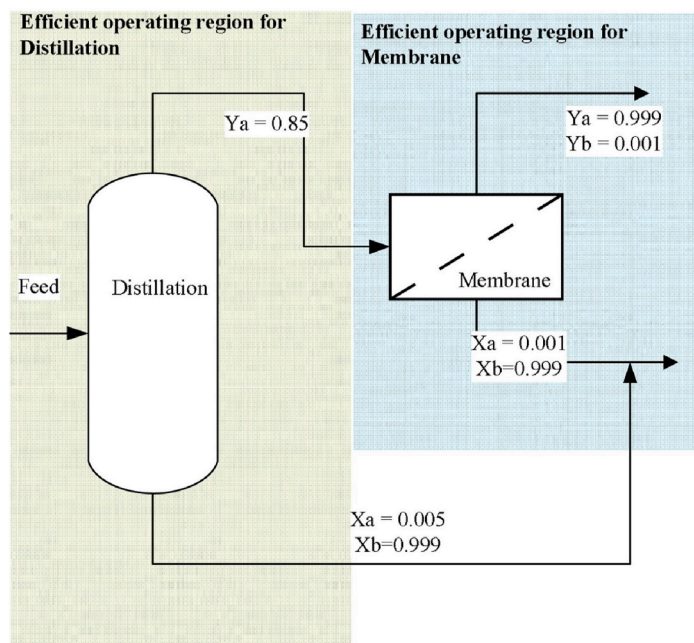
(PV) processes, which are specifically suited for high purity separation with proven applications in chemical and biochemical industry.

However, as for any membrane separation vanishing driving forces limit the application of stand-alone VP or PV processes that are often uneconomical for high throughput and infeasible in achieving high purity of both products. The considered integration of distillation and VP or PV can take advantage of the high throughput and low cost of distillation, as well as the high selectivity and low energy consumption of these membrane separations. Tula et al. [11] took methanol-water

systems as an example to illustrate the benefits of coupling a membrane and a distillation column. Fig. 1(a) shows the concentration-dependent driving force derived by Bek-Pedersen and Gani [12] for the methanol-water system and distillation and membrane separations. It can be seen that distillation and membrane separation have their own effective operating areas, so replacing the separation area of the distillation column at high methanol composition with a very low driving force (consuming large amounts of energy) with a membrane module with higher driving force in this area will ensure both



(a)



(b)

Fig. 1. Hybrid separation of methanol-water systems, (a) driving force for methanol-water systems (distillation and membrane separation), and (b) hybrid separation scheme (see Tula et al. [11]).

separation modes operate in their high-efficiency regions. The resulting hybrid separation scheme is shown in Fig. 1(b). Using the separation effect of membranes can reduce the energy consumption and production costs of specific production processes. Besides the application to close-boiling systems, the integration of distillation and VP or PV is often used in separating azeotropes and removing by-products to promote reversible reactions.

The PV-based distillation process was first used by Binning and James in 1958 to dehydrate isopropanol-ethanol mixtures [13]. However, it was not until the late 1980s that this process was recognized as an attractive alternative to conventional separation processes [14]. The hybrid VP-distillation process has also developed rapidly in recent years [15–19].

In the following, this review will first provide a brief introduction to VP and PV processes from aspects of the mechanism model and membrane materials, followed by an overview from an academic perspective on the integration of distillation and VP or PV for separating azeotropic or close-boiling mixtures, promoting reaction by selectively removing a product, and reducing production load to save energy. Finally, this review gives typical industrial cases of distillation and membrane-coupled separation processes.

2. Membrane separation of VP and PV

The separation principle of PV and VP membranes is different from that of a filtration membrane (i.e., particle filtration, microfiltration, and ultrafiltration). For filtration membranes, the membrane structure has a porous top layer to allow the fluid to pass through the membrane under the applied pressure gradient, while the separation of larger molecules and macromolecules is primarily based on size-exclusion, achieved through the proper pore-size distribution of the membrane material. On the contrary, PV or VP membranes are composed of dense top-layer materials, which are either coated to or synthesized on top of a larger porous support. The separation is based on an adsorption-diffusion mechanism, commonly referred to as the “solution-diffusion” model [20]. The first step of the molecular transport through the membrane is based on the sorption of molecules from the feed into the dense layer material, followed by diffusion through the layer, and finally desorption from the other side of the thick layer to the permeate. This process is illustrated in the schematic diagram in Fig. 2 for a PV/VP membrane:

PV and VP membranes operate on the same basic principle. The difference between them is that the feed fluid in PV is liquid and in VP is steam. The permeate in both cases is steam. The general driving force of material transport for any membrane separation is the chemical potential gradient, which is usually dominated by and simplified to the partial pressure gradient of a substance. To make a component of the feed fluid pass through the PV or VP membrane, the partial pressure of the component on the feed side must be higher than that of the component on the permeate side [21]. Building on the partial pressure difference, the basic form of the membrane flux equation is as follows:

$$J_i = \Pi_i(p_i^F - p_i^V) \quad \text{and} \quad \Pi_i = \frac{P_i}{l} \quad (1)$$

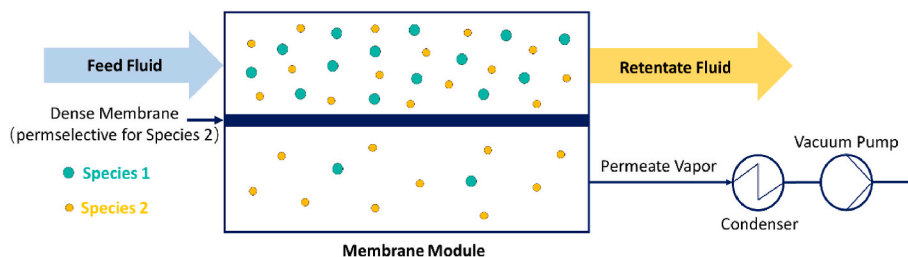


Fig. 2. Schematic diagram of PV or VP membrane separation.

In the formula:

J_i : the molar flux of component i , $\text{kmol}/(\text{m}^2 \cdot \text{s})$;

P_i : the molar permeability of component i , $\text{kmol} \cdot \text{m}/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$;

l : the thickness of the active (dense) layer of the membrane, m ;

Π_i : the molar permeance of component i , $\text{kmol}/(\text{m}^2 \cdot \text{s} \cdot \text{kPa})$; according to the “solution-diffusion” model, it can be defined as the product of the molar solubility coefficient S_i and the molar diffusion coefficient D_i [22]; Since l is unknown or difficult to discern, the permeance (Π_i), the ratio of permeability to thickness, is usually obtained by membrane permeation experiments instead of permeability;

p_i^F : partial pressure of component i on the retentate side of the membrane, kPa ; for VP, when the total feed pressure is not too large, it is approximately expressed by $p_i^F = x_i p^F$, that is the mole fraction x_i of component i on the retentate side multiplied by the total pressure p^F on the retentate side; for PV, $p_i^F = x_i \gamma_i p_i^{\text{sat}}$, that is, the product of the mole fraction x_i of component i on the retentate side, the saturated vapor pressure p_i^{sat} of component i at the temperature of the retentate side and the activity coefficient γ_i of component i on the retentate side, a thermodynamic model is required to calculate γ_i and p_i^{sat} of component i ;

p_i^V : the partial pressure of component i on the permeate side, kPa ; the permeate side is usually evacuated to obtain a high driving force, then no matter VP or PV, it can be expressed by $p_i^V = y_i p^V$, that is, the mole fraction y_i of component i on the permeate side is multiplied by the total pressure p^V on the permeate side;

For commercial membranes of different materials and productions processes, the molar permeance Π_i and the molar permselectivity α are usually used as performance indicators. The selectivity α is expressed by Eq. (2) and depends solely on the chemical system and the material properties of the membrane.

$$\alpha_{12} = \frac{\Pi_1}{\Pi_2} \quad (2)$$

In recent years, with the development of molecular simulation technology, it has been used in the study of membrane separation to describe the static structure of the membrane at the atomic scale and the dynamic behavior of the permeate on a timescale ranging from picoseconds to nanoseconds. This new technology helps people better understand the transport mechanism and the main factors determining permeability and permselectivity of the membrane on a molecular level. Molecular simulation methods mainly include molecular dynamics (MD) simulation and Monte Carlo (MC) calculation.

Currently, the MC method and the extended grand canonical ensemble Monte Carlo (GCMC) method have been widely applied to simulate the sorption of guest molecules in zeolite membranes [23–25]. In addition, MD simulation is often used to calculate the fundamental trajectory of molecular motion, which can simulate the diffusion properties [26,27]. By simulating the sorption and diffusion data of the components, the basic properties such as the flux of the zeolite membrane can be predicted [28]. For instance, Shan et al. [29] first

conducted the MD simulation to examine the effect of the vinyl group on the sorption and diffusion of water and furfural molecules in vinyl-modified polydimethylsiloxane (PDMS) membrane. The simulation results show that an appropriate amount of vinyl group is beneficial to both the sorption and diffusion of water in the membrane, which is verified by experiments.

Although molecular simulation can be used to model the permeation sorption and diffusion aspects, it is necessary to employ a semi-empirical model like formula (1) to benchmark or validate the computational results.

3. Membrane materials for the removal of water or organics by VP or PV

This review provides a brief overview of membrane materials while focusing on the coupling of membrane and distillation. The materials currently used as the selective dense membrane layer for removing water or organics by VP or PV can be clarified into three main types: organic polymeric materials, inorganic materials, and mixed matrix materials. Organic polymeric materials mainly include poly (vinyl alcohol), cellulose polymers, polyimides, other hydrophilic polymers, amorphous perfluoropolymers, emerging organic materials, and layering of polymeric permselective materials. Inorganic materials include zeolites, microporous amorphous inorganic materials, and other inorganic and hybrid materials. Mixed matrix materials mean dispersing nanoscale or microscale particles of the sieving materials into a continuous polymeric phase [21,30].

The candidate membrane materials mentioned above can be evaluated based on the permeance of each component and the permselectivity, which can either be obtained based on a literature survey or by conducting own experiments. In addition, the results from the preliminary evaluation of the potential benefits for the coupling of membrane and distillation can be used to define a target value to screen a suitable membrane material, taking into account the performance of the membrane and an estimated membrane price per area [31].

4. Integration of distillation and VP or PV from an academic perspective

The main applications of distillation and membrane-coupled separation include separating azeotropic or close-boiling mixtures, promoting reaction by selectively removing a product, and reducing production load to save energy. The research conducted within these fields is further summarized in the following subsections.

4.1. Separation of azeotropic or close-boiling mixtures

The methods of using distillation to separate azeotropes include pressure-swing distillation, extractive distillation, and azeotropic distillation, which are all complicated processes that are considered energy-intensive. The separation of close-boiling systems by distillation requires a high reflux ratio or a large number of trays. Since membrane separation is not limited by vapor-liquid equilibrium, it provides a different approach for separating azeotropes or low relative volatility systems.

The integration of distillation and VP or PV for the above-mentioned purpose can be classified into two categories: membrane outside distillation column or inside it. This review summarizes recent studies on the integration of distillation and VP or PV according to these two categories.

4.1.1. VP or PV outside distillation column

According to Sommer and Melin [15], there are four different process configurations of VP or PV coupled with distillation to separate azeotropes or low relative volatility systems, which are illustrated in Fig. 3.

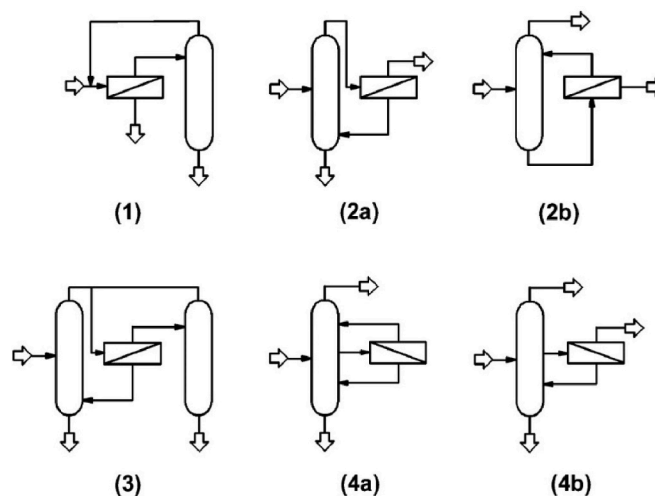


Fig. 3. Process configuration of the integration of distillation and VP or PV: (1) VP or PV before column, (2a, 2b) VP or PV at the top or bottom of the column, (3) VP or PV between columns, (4) VP or PV besides column (see Sommer and Melin [15]).

- (1) The membrane unit is placed in front of the distillation column to break the azeotrope.
- (2) The membrane unit purifies the top (a) or bottom product (b) of the distillation column, obtaining high-purity products by breaking the azeotrope.
- (3) The membrane unit is installed between two columns for the rough separation of azeotropes so that the second column can operate at low energy levels.
- (4) The membrane unit treats the side stream of the distillation column to reduce the theoretical number of stages or reflux ratio of the distillation column for the separation of low relative volatility systems or to break the azeotrope for the separation of azeotropes.

According to the above-mentioned four structural classifications, this review summarizes recent studies on the integration of distillation and VP or PV for the separation of azeotropes or low relative volatility systems.

- (1) VP or PV before distillation column (Fig. 3 (1))

If the composition of a mixture to be separated is close to the azeotropic point, a membrane unit can be applied in front of a distillation column to break the azeotrope. This way, the feed mixture is pre-concentrated, and one azeotrope-forming component of the mixture is selectively removed, allowing for a final purification in the distillation column. As this configuration is only applicable to mixtures with high relative volatility after the azeotropic point, there are only few applications and investigations reported, respectively.

Wan et al. [32] used an alcohol-permeable PV membrane to increase the concentration of acetone, butanol, and ethanol in the fermentation broth. After phase separation, an organic phase with little water content was obtained, during which the azeotropic point of butanol and water had been exceeded. The organic phase was distilled to obtain high-purity butanol.

Facing the problem that unreacted ethanol and ethyl tertiary butyl ether (ETBE) form an azeotrope in the production process of ETBE, Norkobilov et al. [33] proposed that a PV unit can be placed after the reactor to remove unreacted ethanol and return it to the ethanol feed location of the reactor, then the retentate can be fed to the subsequent distillation column to separate ETBE and C4.

(2) VP or PV at the top of the distillation column (Fig. 3 (2a))

A membrane unit at the top of a distillation column is used for mixtures having a temperature minimum azeotrope. Obtaining the azeotropic composition in the distillate stream, VP or PV allows for a final purification, especially if the azeotropic point occurs at high concentrations of the low boiler. The most prominent example among others is the dehydration of ethanol, which was subject to several studies [31,34–48]. Some of these are summarized in the following.

Li et al. [46] placed a VP module at the top of the distillation column to split the ethanol and water azeotrope, obtaining high-purity ethanol (99.6 wt% or 99.95 wt%). In addition, the important operating parameters, such as the top ethanol concentration and the top pressure of the distillation column, were optimized. Gao et al. [47] designed a pilot plant for NaA molecular sieve membrane dehydration to separate ethanol from water. They investigated the effects of raw water content, reflux ratio, and collection amount on the product purity of the column and the permeation flux of the VP device. Roth et al. [40] also investigated the separation of ethanol and water by a range of hybrid process configurations with the aid of experimentally validated rate-based models, including VP-assisted distillation. Comparing this process with other combinations, such as distillation and adsorption, VP and adsorption or a combination of all three unit operations for different capacities and product compositions, indicated large potential of the VP-assisted distillation for high ethanol purities (99.6 wt%), while further purification by adsorption is advised to reach even higher purities (99.95 wt%).

Scharzec et al. [31] also investigated ethanol dehydration by a PV-assisted distillation process to illustrate the usefulness of a systematic design approach. The proposed 5-step approach starts with the synthesis of different process configurations and an optimization-based evaluation of the minimum energy demand of these process configurations, assuming an ideal or nearly ideal membrane separation. Thereby the potential benefit of the membrane-assisted process can be evaluated prior to any experiments. The results of this evaluation for a feed stream with 10 mol% ethanol are illustrated in Fig. 4, showing that the PV-assisted process requires substantially less energy than a competing heteroazeotropic distillation process with cyclohexane as entrainer if the top product is not exceeding purity of 86 mol%. It further indicates that the selectivity of the PV membrane is not that critical for this specific separation.

In case of a sufficient potential of the PV-assisted process, a suitable membrane has to be identified, experimentally characterized, and an

economic assessment by means of an optimization-based evaluation is performed, considering potential means of process intensification, such as the use of heat-integrated membrane modules [49]. This is further illustrated by Scharzec et al. [50] for the separation of a ternary mixture of tetrahydrofuran, methanol, and water. Further examples of separating an azeotropic mixture by combining a simple distillation column with a membrane processing the distillate stream can be found in Refs. [51–61].

Furthermore, VP or PV can be combined with a reactive distillation column, e.g., to overcome the chemical equilibrium. Therefore, Holtbruegge et al. [62] placed a VP module at the top of a reactive distillation column, which was used to accomplish azeotrope separation. In the reactive distillation column, propylene carbonate (PC) and methanol (MeOH) were *trans*-esterified to synthesize dimethyl carbonate (DMC) and propylene glycol (PG). At the top of the column, a binary azeotrope of MeOH and DMC was obtained, the VP module removed DMC, and the retentate was returned to the column. Mihai et al. [63] and Buchaly et al. [6] placed a PV module at the top of the reactive distillation column for esterification of propionic acid and *n*-propanol. The azeotrope of *n*-propanol and water at the top of the column entered the PV module for dehydration to obtain high-concentration *n*-propanol, which was recycled back to the *n*-propanol feed position, significantly reducing the consumption of fresh *n*-propanol by about 40%. Harvianto et al. [64] studied a highly selective PV membrane coupled to a reactive distillation process to produce butyl acetate and methanol through the *trans*-esterification of methyl acetate and butanol. The PV module placed at the top of the distillation column was used to remove methanol to break the azeotrope of methanol and methyl acetate, thereby obtaining high-purity methyl acetate and high-purity methanol. High-purity methyl acetate was recycled back to the methyl acetate feed position, leading to high conversion in the reactive distillation column, which can reduce total annual cost (TAC) by 60% compared with the traditional reactive distillation column plus the de-methanol column. There are similar studies on the separation of azeotropes by placing VP or PV modules at the top of reactive distillation columns [65–68].

Early research on distillation and membrane coupling often linked membrane modules and distillation columns as a series of simple unit operations. This neglects the significant reduction in energy that can be accomplished by thermally integrated processes. While it has to be considered that the heat of condensation for the low pressure permeate streams is usually lost and may even be expensive to remove by sub-ambient cooling, special means for heat integration can significantly enhance the performance of the membrane assisted process, such as the

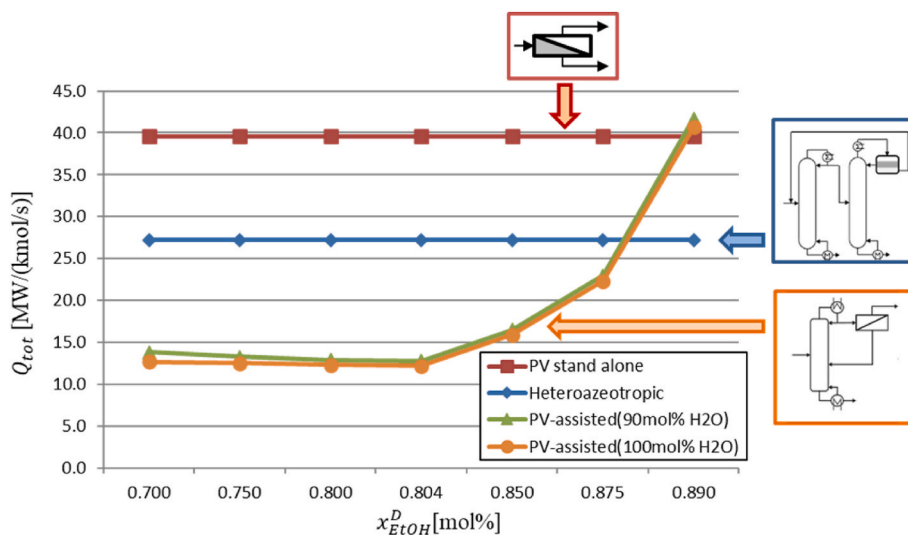


Fig. 4. Evaluation of PV-assisted distillation for ethanol dehydration based on an ideal (100 mol% H₂O) and nearly ideal (90 mol% H₂O) hydrophilic PV separation for a feed with 10 mol% ethanol (see Scharzec et al. [31]).

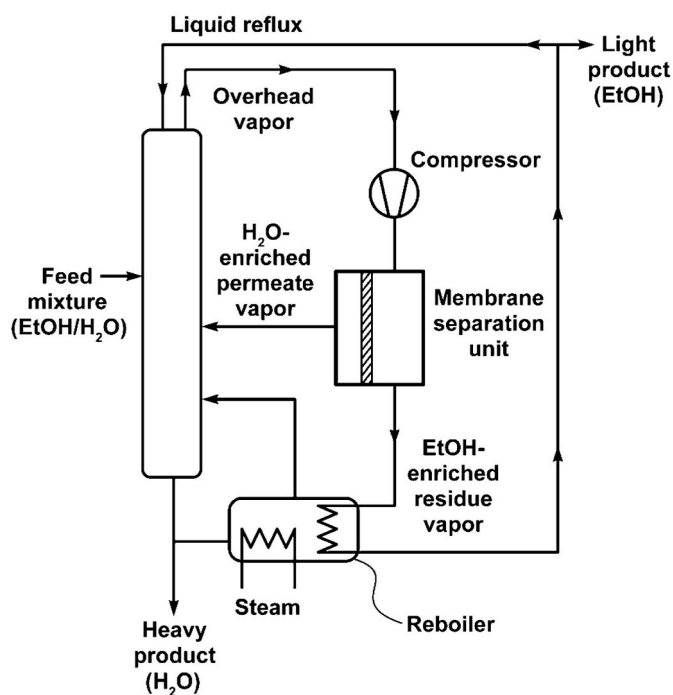


Fig. 5. Schematic diagram of a thermally integrated distillation-VP hybrid process (see Huang et al. [17]).

heat integrated membrane-modules for pervaporation proposed by Del Pozo Gomez et al., [49,69]. Besides, Huang et al. [17] developed a new thermally-integrated distillation-VP hybrid process that combines vapor permeation and vapor recompression. The schematic diagram is depicted in Fig. 5. They illustrate the process for two kinds of organic solvent and water separation processes that are ethanol (light component)/water (heavy component) separation and acetic acid (heavy component)/water (light component) separation. In both cases, the heat-integrated process can reduce the energy consumption of the separation to half that of the traditional distillation technology. Yamaki et al. [18] thermally integrated the retentate of the VP module with individual trays and the reboiler of the distillation column, achieving less energy consumption than the distillation-VP hybrid process without any thermal integration. Li et al. [70] invented a method of thermally integrating distillation and VP to recover 2-methyltetrahydrofuran. The

product extracted from the VP module was in the state of steam, and the efficient thermal integration was realized by its heat exchange with the liquid in the bottom of the column, significantly saving steam consumption by 40–60% compared with the traditional process. Zhou et al. [71] invented an energy-saving distillation-PV coupling method for the separation of organic azeotrope systems without a condenser at the top of a column. The PV module was used as a condenser to cool the steam generated from the top of the column by utilizing the heat-absorbing characteristic in the PV process, which effectively reduced the energy consumption of the column condenser. Similar thermal integration research and further advanced exergy and energy efficiency analysis can refer to in the literature [72–79].

Obtaining high-purity organics by distillation from low-concentration organic solutions such as bioethanol (ethanol is produced from syngas or sugar substrates originating in lignocellulosic biomass or directly from algae, with ethanol concentrations below 5 wt % [80–82]) is energy-intensive. Membrane-assisted vapor stripping (MAVS) technology (Fig. 6 shows the schematic diagram of a MAVS unit for bioethanol production [16]) can significantly reduce energy consumption and obtain high-purity organic products through membrane separation of azeotropes as demonstrated in several studies [16,83–89]. For instance, Zhou et al. [89] proposed a three-column and two-membrane process for preparing fuel ethanol from the biological mash, which can reasonably distribute the fluid flow, make full use of fluid heat, and further reduce the size of the column as well as the temperature difference between the column and the membrane separation device, to achieve the purpose of reducing the energy consumption of the system. The advantage of the MAVS process was also illustrated by a more general superstructure optimization approach by Kuhlmann et al. [90], while Gudena et al. [91] further illustrated additional intensification by means of a HiGee Stripper-membrane system that allows for compact process implementation.

Regarding the optimization of distillation-VP hybrid processes, most early studies performed a simulation-based assessment by means of sensitivity analysis and single factor modifications, ignoring the interaction between the structure and operating parameters of the mixing process. Besides the already mentioned optimization-based methods [31,50,92], other methods for design optimization have been considered [93–95]. One possible solution proposed by Xiao et al. [94] is to use the Response Surface Method (RSM), which is widely used to analyze the influence of multiple factors and their interactions. They used this method to optimize the distillation-VP hybrid process of preparing high-purity isopropanol, and the optimal value was obtained (the

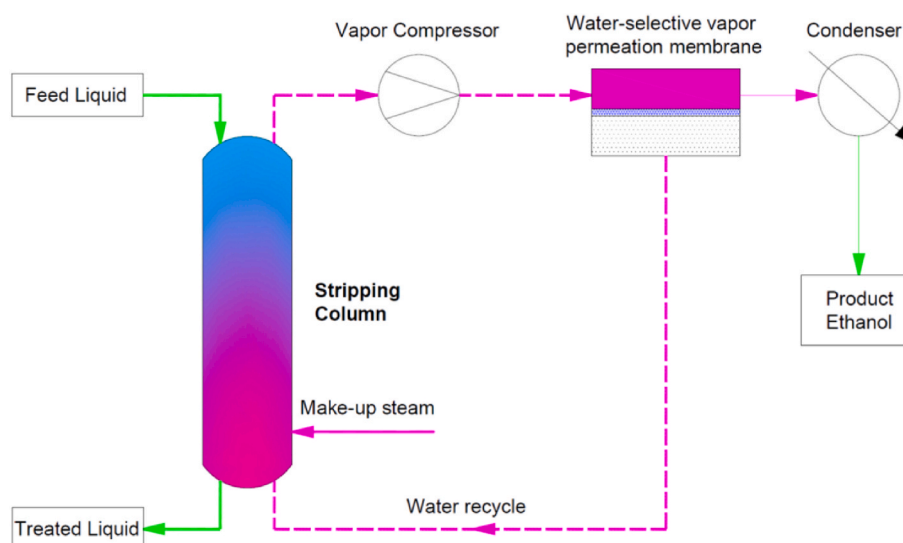


Fig. 6. Schematic diagram of membrane-assisted vapor stripping (MAVS) for bioethanol production.

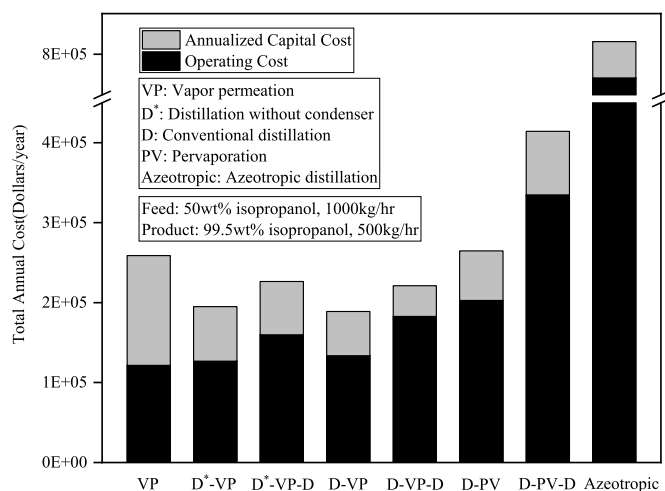


Fig. 7. Comparison of the total annual cost for different IPA dehydration processes.

detailed process was implemented in three steps, a. Plackett-Burman (PB) experimental design to find significant parameters, b. Optimization by steepest ascent path experiment to find the center point of Box-Behnken design (BBD) for RSM, c. Optimization by BBD to do a polynomial fit and get the optimal value). Harvianto et al. [95] studied the design and optimization of distillation and VP hybrid process for cost-effective isopropanol dehydration. RSM was used for optimization. Several coupling structures were proposed, among which the D-V-P structure achieves the lowest total annual cost, saving almost 77% compared to azeotropic distillation, as seen in Fig. 7.

(3) VP or PV at the bottom of the distillation column (Fig. 3 (2b))

VP or PV in the bottom of a distillation column can be used if the mixture to be separated exhibits a maximum-boiling azeotrope. According to Kiva et al. [96], the occurrence of azeotropes with that behavior is much less likely compared to mixtures with a temperature-minimum azeotrope. However, still some applications are reported in the literature, e.g., for close-boiling mixtures. Szilagy et al. [97] designed a process for the removal of ethanol and methanol from wastewater in the pharmaceutical industry. The second distillation column was combined with a PV module to realize the purification of ethanol and methanol. The ethanol-water mixtures extracted from the bottom of the column were dehydrated by a PV module to obtain 99.5 wt % ethanol. Lv et al. [98] proposed a process for the separation of ethylenediamine-water azeotropes by using a PV module to treat the bottom product (the highest azeotrope of ethylenediamine and water) of the ethylenediamine-water distillation column. High-purity ethylenediamine can be obtained from the retentate side of the PV module, while water is produced as the permeate that was further returned to the distillation column. Servel et al. [99] investigated the separation of acetic acid and water whose vapor-liquid equilibrium is very narrow. They proposed that a PV module should be placed according to the composition of the feed either at the bottom of the column and used for dehydration when the concentration of acetic acid in the feed is high, or overhead the column and used for removing acetic acid, if the concentration of water in the feed is high.

(4) VP or PV between distillation columns (Fig. 3 (3))

Sommer and Melin [15] proposed that this structure is most suitable when a very high purity (ppm level) product needs to be obtained. Because, in this case, the partial pressure difference of the permeate across the VP or PV module is very small, so the membrane area required

will increase significantly. Under this circumstance, the azeotrope can be roughly separated by the membrane, and the purification is achieved in the subsequent column, which can considerably reduce the investment cost. Zhou [100] invented an industrial equipment for the production of high-purity ethylene glycol dimethyl ether, which mainly includes PV membrane, distillation system before PV, and distillation system after PV. A PV module was used to break the azeotrope and produce high-purity ethylene glycol dimethyl ether with a water content of less than 500 ppm, which is obtained at the bottom of the distillation column after PV. Further studies on this topic can be found in Refs. [101–103]. As previously mentioned in the study of Roth et al. [40], purification may also be accomplished effectively by means of an additional adsorption column instead of a distillation column.

The main problem with the separation of THF and water by conventional pressure swing distillation is that a large amount of fluid should be recycled to the atmospheric column, which increases the physical size and thermal requirements of the column. Pribic et al. [104] proposed that PV can be used to treat the tetrahydrofuran-water azeotrope from the atmospheric column and separate the binary azeotrope into a water-rich permeate and a tetrahydrofuran-rich retentate that is fed to the high-pressure column, thus solving this problem. With this configuration, the circulating flow becomes smaller, saving energy and reducing the size of the atmospheric column.

As mentioned above, a thermally integrated process can save significant energy. The traditional PV process requires the supply of external energy to maintain a constant temperature of retentate, and heat integration can improve the energy efficiency of the PV process. Zong et al. [105] designed a heat-integrated PV–distillation hybrid system for the separation of an azeotropic methyl acetate-methanol mixture using a low-temperature residual stream to cool the top vapor of the column, which can lower the energy consumption by 24% compared to that via pressurized distillation with heat integration.

(5) VP or PV beside distillation column (Fig. 3 (4a, 4b))

This structure is suitable for separating azeotropes, especially ideal for separating ternary mixtures containing azeotropes. In this case, the VP or PV module process the side stream drawn from the distillation column to break the azeotrope and obtain a high-purity component that can form azeotropes with the other one or two components. Finally, the other two high-purity components can be obtained at the top and bottom of the distillation column, respectively. In addition, when separating low relative volatility systems, the excellent separation effect of the VP or PV module can save the number of theoretical stages or heat load of the distillation column.

A potential application investigated by Gorak et al. [106] considers the separation of a mixture of acetone, isopropanol, and water. In this system, isopropanol-water forms an azeotrope, which results in a distillation boundary that extends to the low-boiler acetone. The authors placed the PV module in a side stream connection with the distillation column to selectively remove water from the side stream, thereby obtaining acetone at the top of the column and isopropanol at the bottom of the column, effectively breaking the azeotrope. These studies were further extended by means of experiments and model-based assessment, providing detailed rate-based models [107,108].

The formation of an azeotrope between unreacted ethanol and ETBE in ETBE production is a difficult problem to overcome. Norkobilov et al. [109] used the PV module to process the side stream drawn from the debutanizer, and the permeate (high-purity ethanol) was recycled back to the reactor, while the retentate (ETBE + ethanol) was recycled back to the debutanizer, so that ETBE with a purity of 95.2 wt% was obtained at the bottom of the debutanizer. It was concluded that compared with the traditional process (reactor + debutanizer + pressure swing distillation), the new process cancels out the pressure swing distillation and the heating load was saved by 52% while the cooling load was saved by 49%. In the model-based evaluation of Skiborowski et al. [92], the

separation of the ternary mixture of methyl *tert*-butyl ether (MTBE), *n*-butene, and methanol, which exhibits two binary azeotropes, was investigated for a process for which a PV membrane overcomes the MTBE-methanol azeotrope obtaining methanol in the retentate stream, while *n*-butene is obtained at the top of the distillation column and MTBE at the bottom.

Singh and Rangaiah [110] proposed a novel double-effect distillation (DED)-VP process for bioethanol recovery, in which the single distillation column in the distillation-VP process was replaced by two columns, namely the low-pressure column (LPC) and high-pressure column (HPC) in a parallel configuration. The cooled side streams of LPC and HPC were mixed and sent to the two-stage VP unit to break the azeotrope for obtaining high-purity ethanol. The optimized DED-VP process reduces TAC by 11% compared to the optimized distillation -VP process.

Babaie and Esfahany [111] proposed a new process for the production of ETBE by placing a PV module (series-parallel form) on one side of the reactive dividing wall column (RWDC) (with feed splitting and heat integration). The minimum azeotrope formed by ETBE and ethanol can be eliminated by the PV module, which can significantly reduce the number of trays in the main and pre-fractionator sections in RWDC. This process reduces TAC by 59% compared to the traditional ETBE production process. A similar study [112] also showed that placing a PV module on the side of the distillation column or reactive distillation column is a better process for ETBE production.

For the separation of low relative volatility systems, this structure (VP or PV beside the distillation column) can significantly reduce the number of theoretical stages or reflux ratio of the distillation column. The change in the operation line of the distillation column due to the addition of the membrane can be seen in Fig. 8 [113].

Zarca et al. [114] used a VP module coupled with distillation to separate a mixture of propane and propylene, which is considered a particularly energy-intensive separation. The propane/propylene mixture is first separated by a VP module and then purified by distillation, which can be classified as a series configuration. Compared to direct distillation, 10–50% of the total operating cost can be saved. Ploegmakers et al. [115] investigated two separation processes for ethylene and ethane that consider placing the VP module in front of the distillation column (series configuration) and placing it after the distillation column (parallel configuration), indicating that especially the series configuration is more economic. Similar studies were conducted by Park et al. [116], who investigated a different system: a mixture of propane and propylene. Further examples of separating low relative volatility systems using such structures can be found in Refs. [117–119].

Similar to the study of Huang et al. [17], the use of heat pump technology has been proposed for the integration of distillation and VP or PV for separation of near boiling point mixtures as an effective means for improving the energy efficiency. Park et al. [120] applied heat pump technology to VP and distillation coupled process (series configuration)

for the separation of propylene and propane, which has a huge advantage in terms of energy and economic savings.

4.1.2. VP or PV inside the distillation column

In addition to the above four typical structures, more recently, a novel type of integration has been proposed, which considers a direct integration of the membrane inside the distillation column, which can also break azeotropes [121]. Such a solution is representative of a hybrid separation, as defined by Stankiewicz [122]. In a series of publications, Leon and Fontalvo [123–126] presented theoretical research and experimental verification of the hybrid separation concept with the membrane inside the distillation column. They confirmed the feasibility of the PV-inside-distillation column configuration crossing the distillation boundary formed by the azeotropic point through the batch distillation experiments for separating the ethanol-isopropanol-water mixture [123]. Then a series of continuous separation experiments of the ethanol-isopropanol-water mixture in an experimental glass column coupled with the PV membrane was carried out, verifying this technology's theory [124].

Haelssig et al. [127,128] also proposed a membrane dephlegmation process for the separation of an ethanol-water azeotrope, which can replace the ethanol concentration column and the dehydration system in the bio-based ethanol recovery process. The schematic diagram of this membrane dephlegmation process can be seen in Fig. 9. The hybrid separation that integrates distillation and PV improves the efficiency of the distillation process and the total energy efficiency of the bio-based ethanol production process.

Leon and Fontalvo [129] studied a distillation–PV hybrid process in a single unit column with a membrane packing section inside the distillation column for the separation of a ternary mixture of acetone-isopropanol-water. A simplified model based on phase equilibria and membrane selectivity was derived, and conceptual feasibility on separation trajectories was shown. While the concept of the integrated hybrid separation is particularly intriguing, it has to be considered that this tight integration also imposes severe constraints on the sizing and operating conditions, which may limit the potential of the hybrid separation and mandates a direct comparison with external integration of a hybrid membrane assisted processes, which is yet missing.

4.2. Promoting reaction by selective product removal

One interesting application of membranes in combination with reactions is the selective removal of a reaction product, thereby shifting the chemical equilibrium of the reaction and improving the conversion rate of the reaction. The following review of current research focuses on the coupling of reactor-distillation-membrane as well as the coupling of reactive distillation and membranes, while the reader is referred to the extensive literature on membrane reactors for integrations without distillation.

Boontawan [130] proposed a continuous stirred tank reactor-distillation-membrane hybrid structure for the esterification of succinic acid into diethyl succinate. A high-efficiency fractionation column was set on the top of the tank reactor, and the conversion rate exceeded the thermodynamic equilibrium conversion by continuously removing the water in the reactor as a fraction. In addition, the fraction was successfully dehydrated by vapor permeation through the commercial hydrophilic polymer membrane, and then the dehydrated ethanol was refluxed into the tank reactor to further promote the esterification reaction, as shown in the schematic diagram (Fig. 10). Gu et al. [131] also proposed a continuous stirred tank reactor-distillation-membrane coupling process for the production of diethyl maleate, for which water in the esterification reaction system was continuously removed through vapor permeation membrane. Therefore, the reaction was promoted to the direction of the formation of diethyl maleate, and the conversion rate of the reaction was effectively improved. The new hybrid process

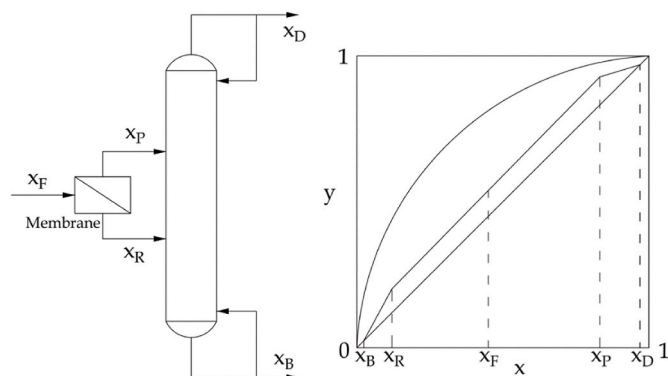


Fig. 8. The operation line of the distillation column with the addition of membrane beside the column.

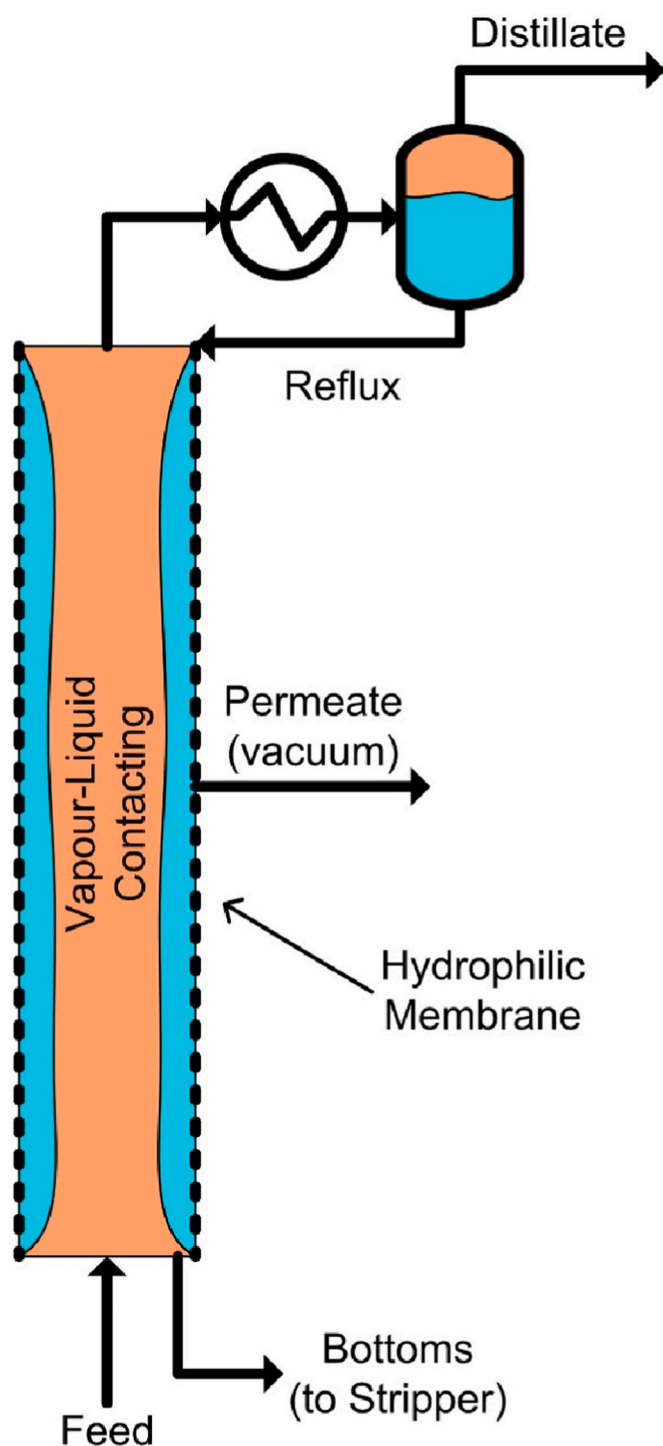


Fig. 9. Magnified view of the proposed distillation-PV hybrid process (see Haelssig et al. [127]).

occupies a small area, is easy to scale, and has low energy consumption. When the water content in the tank reactor was below 0.13 wt%, the reaction was stopped, and the reaction residue was distilled to remove and recover ethanol. Other such studies consider a similar configuration [132,133].

Agirre et al. [134] proposed a coupled process of tubular reactor-membrane-distillation for the continuous production of 1, 1-diethoxybutane. The by-product water was removed from the mixture at the outlet of the tubular reactor by a PV module. The high-efficient removal of water can avoid azeotrope formation in the

downstream distillation column. The dehydrated mixture entered the subsequent distillation system, and the reaction product was obtained at the bottom of the distillation column, while the unreacted substrate was recovered at the top of the column and further recycled to the reactor. The conversion of this process is close to 100%.

Reactive distillation is a process intensification method to break through chemical reaction equilibrium, and its coupling with the membrane can further improve the conversion rate of a reversible reaction. Wang et al. [135] used the synthesis of ETBE as a model system to research the coupling of reactive distillation and membrane separation. The PV module was placed at the bottom of the reactive distillation column. After continuously separating most of the by-product water from the bottom fraction of the column by the PV module, the retentate was returned to the reboiler of the reactive distillation column, which increased the concentration of reactants in the reactive distillation column, thereby improving the efficiency of reactive distillation. Lv et al. [136] also applied a similar method to the reactive distillation of ethyl acetate, and it was concluded that the ethanol conversion was increased from 81.3% to 84.8%. Arpornwichanop et al. [137] proposed the integration of a PV module in a side stream of tert-amyl ethyl ether (TAAE) reactive distillation column to remove water and increase the conversion in the column selectively. It was found that due to the removal of by-product water, the conversion of tert-amyl alcohol (TAA) and the purity of TAAE product increased compared with the conventional reactive distillation. Tang et al. [138] further proposed a hybrid process for the integration of reactive distillation and PV to produce ethyl acetate. The PV module was placed on the top of the reactive distillation column. The water produced by the esterification reaction was partially drawn from the side of the reactive distillation column and partially removed by the PV module to promote the esterification reaction so that the reactants were completely converted.

Following the concept of a hybrid separation, Aiouache and Goto [139] first proposed to put the membrane in the reactive distillation column and designed an experimental device. They inserted a zeolite NaA membrane tube into an experimental apparatus of the reactive distillation column and carried out the etherification reaction of tert-amyl alcohol and ethanol. Due to the removal of by-product water, the yield of TAAE was increased by 10% compared with no NaA membrane tube insertion.

Han et al. [19] first designed a pilot-scale device of the reactive distillation column with a membrane inside and published a patent [140]. The schematic diagram is depicted in Fig. 11. They developed an inter-integration reactive distillation with vapor permeation (R-VP-D) process, which integrated reaction, vapor permeation, and distillation into one single unit for the esterification of levulinic acid and ethanol, and the proposed process was validated in the pilot-scale experiments. This new R-VP-D process increased the conversion rate of levulinic acid by 21.9% compared with the reactive distillation (RD) process without the VP module. It removed the by-product water about 53.6% from the VP module. The R-VP-D process solves the problems of equilibrium-limited reaction and separation of an azeotrope that are difficult to deal with by traditional methods and has an excellent industrial application prospect in the field of process intensification. In the same research group, Wu et al. [141] performed a simulation-based assessment of the experiments of Han et al. [19] utilizing a 2-dim Aspen Custom Model. The model was verified by the experimental results, providing a basis for the design and optimization of the subsequent R-VP-D processes of different systems.

4.3. Application for reducing production load and saving energy

In addition to the above two main application fields of the integration of distillation and VP or PV, there are also many studies [142–163] on solely using membranes to separate organics or water to reduce distillation load or the amount of cycles in the process, thereby reducing energy consumption and production cost. For instance, Li et al. [143]

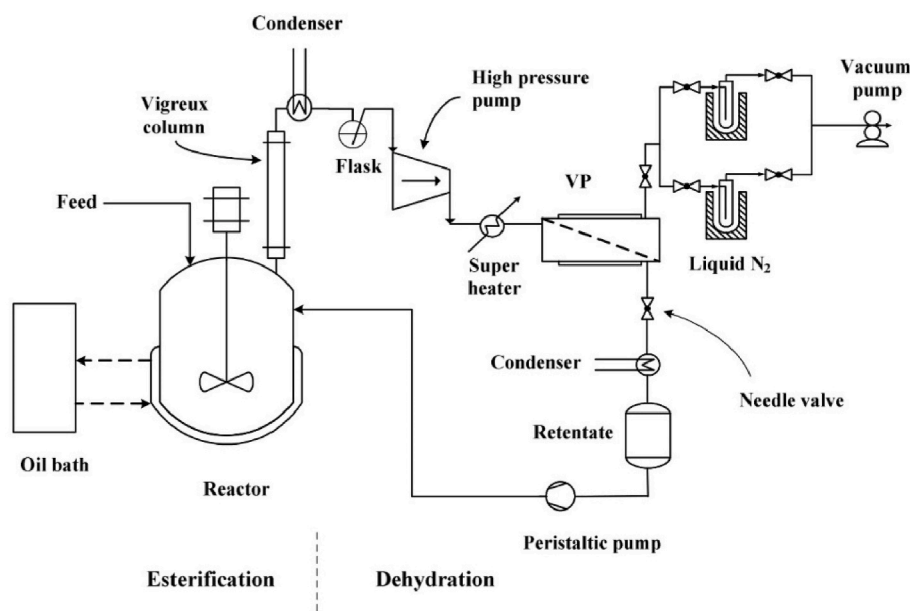


Fig. 10. The flowchart of the continuous stirred tank reactor-distillation-membrane hybrid process (see Boontawan [130]).

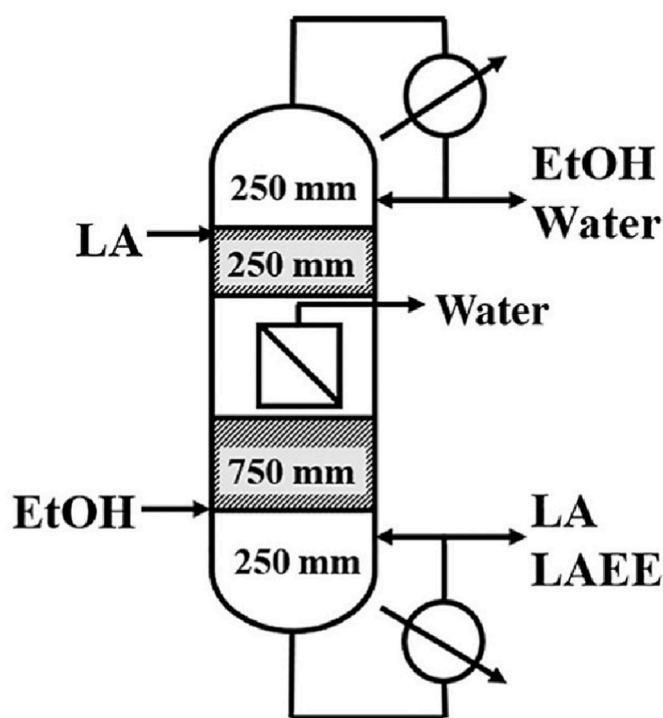


Fig. 11. Conceptual diagram of reactive-vapor permeation-distillation (R-VP-D) process (see Han et al. [19]).

designed a reactive dividing-wall distillation (RDWD)-PV process for the production of main-product *n*-butyl acetate and by-product methanol by transesterification of MM80 (35 mol% methanol, 65 mol% methyl acetate). Compared with the traditional reactive distillation (RD)-de-methanol column (MC) process, the newly designed process saved 40.8% of operating costs, 32.6% of TAC, and 48.77% of CO₂ emissions, mainly because most methanol product was recovered by PV process, which reduced the circulating flow rate and reflux ratio of the reactive distillation column, thereby reducing the heat load of the reboiler. In addition, setting the reactive distillation column as a dividing wall

column can further reduce the investment cost of the distillation column and the condenser. Zhang et al. [145] separated the azeotrope of a cyclohexane-IPA-water mixture by using a PV-assisted extractive distillation process. Compared with the basic process, the CO₂ emissions of the PV-assisted extractive distillation process were reduced by 15.09%, and the PV module was used to replace the extractant recovery column in the basic process. Based on the optimized pressure swing reactive distillation process (PSRD, as shown in Fig. 12) reported by Huang et al. [164] for the intensified synthesis of dimethyl carbonate (DMC), Li et al. [154] proposed a novel PV-assisted pressure swing reactive distillation process (PSRD-PV, as shown in Fig. 13). Compared with the PSRD process, 42.22% TAC savings and 31.36% energy savings can be achieved by the new PSRD-PV process, which was ascribed to the PV module that was set between the reactive distillation (RD) column and the high pressure (HP) column. The PV module pre-separated the mixture of methanol and DMC from the top of the RD column, thereby significantly reducing the load of the downstream HP column. Dai et al. [159] improved the traditional extractive distillation process for separating di-isopropyl ether/isopropanol/water mixture using a PV membrane. The original ethylene glycol and water separation towers were replaced by a PV dehydration membrane, which reduced TAC by 22.3%. In addition, the new process has an advantage over extractive distillation on enabling the environment and reducing human toxicity. Regarding the production of acetone-butanol-ethanol (ABE) from municipal solid waste (MSW), purification of ABE is the most difficult and expensive part because of the low concentrations of the products in the ABE fermentation in which water makes up the majority. Ashani et al. [162] developed a novel process in which PV and gas stripping systems were right after the fermentation reactor. A large fraction of water in ABE fermentation was separated by the PV module, which significantly simplified the downstream purification unit, and the number of the distillation column was reduced from six in the traditional process to two. This new process reduced the payout periods of the traditional process from 15.9 years to 2.9 years.

5. Integration of distillation and VP or PV from an industrial perspective

There are many industrial examples of the integration of distillation with PV and VP around the world [21]. This review focuses on hybrid processes for the integration of distillation and membrane separation

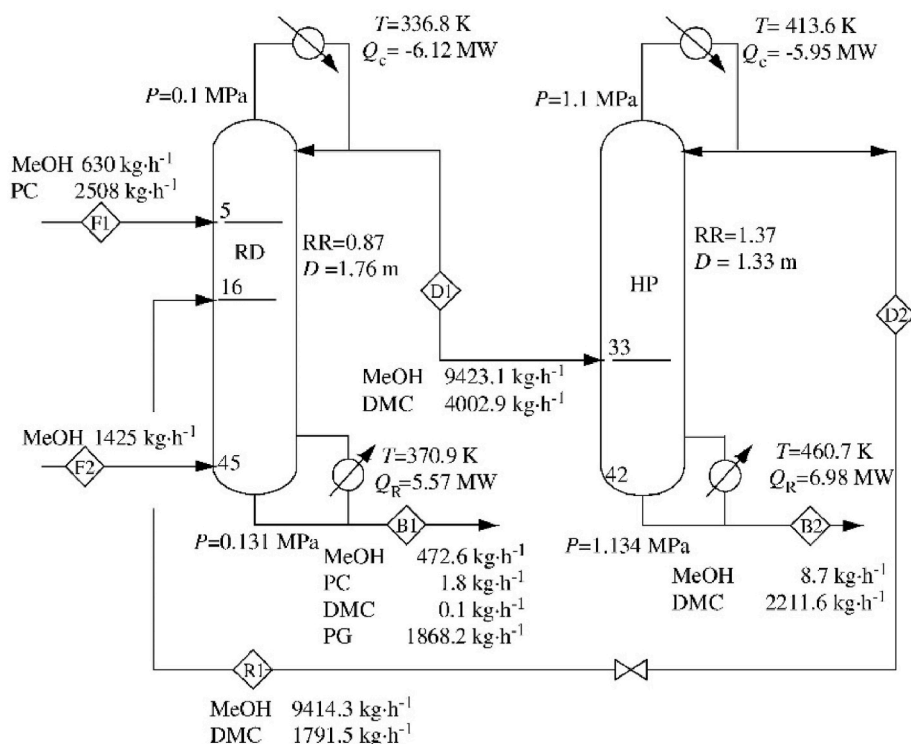


Fig. 12. Flowsheet of the base case optimal PSRD process (see Huang et al. [164]).

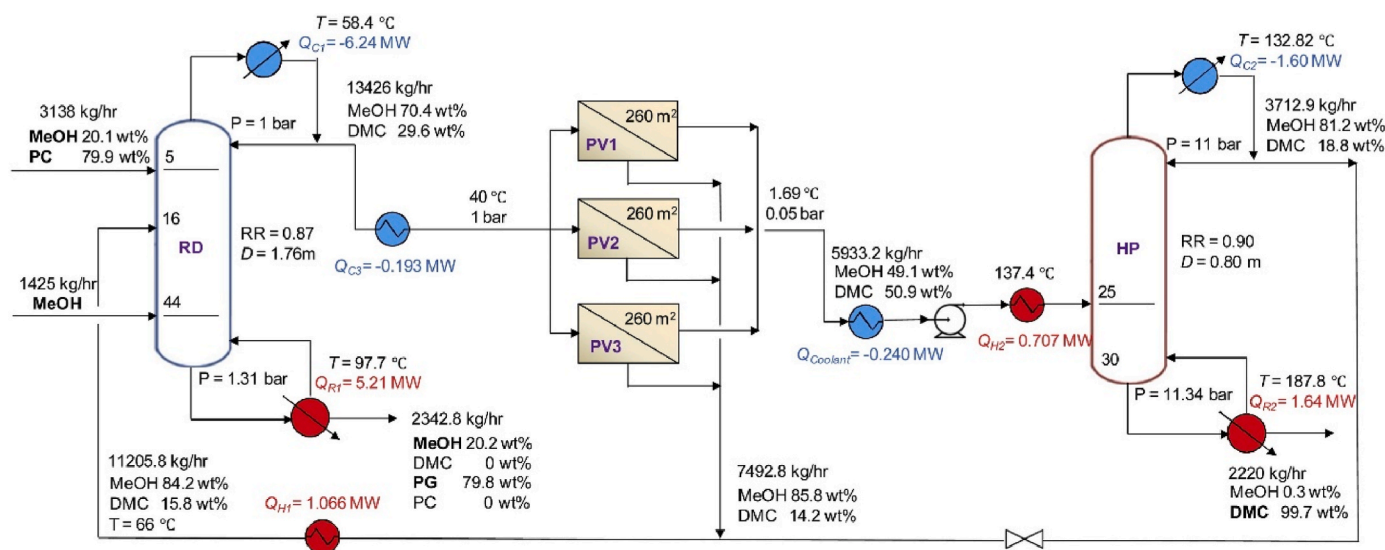


Fig. 13. Flowsheet of the optimized novel PSRD-PV process (see Li et al. [154]).

that have been installed in China. At present, distillation and membrane coupling devices that have been installed are mainly used to separate azeotropic mixtures.

The water-phase by-products of Fischer-Tropsch synthesis can be separated to obtain low-carbon mixed alcohols, including the mixture of methanol, ethanol, propanol, butanol, amyl alcohol, hexanol, heptanol, octanol, etc. and water, all but methanol form an azeotrope with water. A total of seven distillation columns and five circulations are set up for the traditional extractive distillation process of the recovery of mixed alcohol, which is lengthy and challenging to control. Since the PV dehydration of the molecular sieve membrane is not limited by the vapor-liquid equilibrium, the coupling of distillation and molecular sieve membrane can simplify the traditional process. At the beginning of

2015, Shanxi Yanchang Petroleum (Group) Co., Ltd. took the lead in adopting the molecular sieve membrane dehydration technology of Dalian Hyster Technology Co., Ltd. to build an industrial demonstration plant of molecular sieve membrane dehydration with a scale of 1000 t/a mixed alcohols in the Fischer-Tropsch synthesis project. This industrial demonstration plant was integrated with an existing distillation unit, as shown in Fig. 14, and the plant was equipped with eight molecular sieve membrane modules with a total membrane area of 67 m². The series configuration of molecular sieve membrane modules was applied for the dehydration of mixed alcohols. After industrial transformation, the number of main equipment of the new process was reduced to five with no circulation loop, thereby reducing the total heat loads of the new process to 69.4% of the traditional process [165].

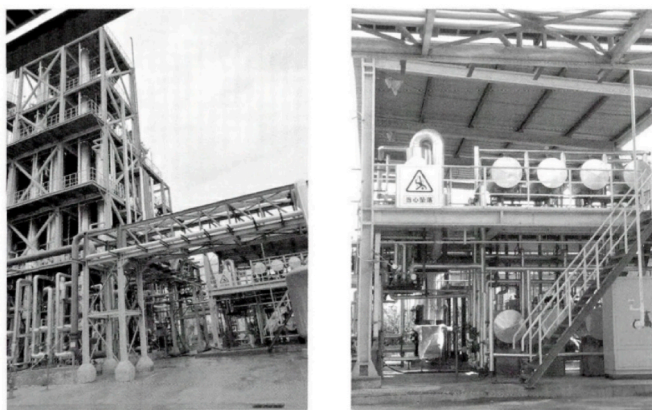


Fig. 14. The equipment installation photos of an industrial demonstration plant of the integration of molecular sieve membrane and distillation (see Hu et al. [165]).

Isopropanol is widely used as a solvent or extractant in the pharmaceutical industry. However, isopropanol and water form an azeotrope (12.6 wt% water, under normal pressure), making it difficult to separate. Traditional recovery of isopropanol adopts azeotropic distillation or extraction process with high energy consumption. The dehydration process of molecular sieve adsorption can't be industrially applied due to the high water-content in the isopropanol aqueous solution. Jiangsu Jiutian High-Tech Co., Ltd. designed a 3000 t/a isopropanol separation plant with the integration of distillation and molecular sieve membrane for Shenyang Sanjiu Pharmaceutical Co., Ltd. The isopropanol vapor (water content ~12 wt%) was dehydrated by the VP module to obtain the isopropanol product. A similar coupling plant designed by Jiangsu Jiutian High-Tech Co., Ltd. is the 8000t/a distillation-molecular sieve membrane coupling device for separating ethanol and water. The VP module was set at the top of the distillation column to break the azeotrope of ethanol and water. The operating cost was reduced by 31.2% compared to traditional extractive distillation.

In the traditional process of synthesizing and refining acetonitrile by the acetic amination method, acetonitrile is obtained by the ammonification of acetic acid and ammonia gas. The crude product obtained after the reaction contains acetonitrile, water, and a small amount of ammonia. After removing ammonia by a two-stage absorption tower, the crude product enters the acetonitrile concentration column, the negative pressure column, and the positive pressure column in turn to obtain acetonitrile product. In this process, the azeotrope formed by acetonitrile and water (12.6 wt% water, under normal pressure) is broken by pressure swing distillation. Jiangsu Jiutian High-tech Co., Ltd. designed a 10kt/a acetonitrile separation plant with the integration of distillation and molecular sieve membrane for Shandong Huihai Company, as seen in Fig. 15. The 78 wt% acetonitrile vapor stream from the top of the acetonitrile concentration column entered the VP module for dehydration, thus breaking the azeotrope, then entered the acetonitrile atmospheric distillation column. This new process is simple with a high safety factor, high energy efficiency, and a small amount of liquid circulation, which leads to low operating energy consumption (the steam consumption of the traditional process is 4 t/t, and that of the new process is 1.6–2 t/t).

6. Conclusion

Compared with traditional pressure swing distillation, extractive distillation or azeotropic distillation, the integration of distillation and pervaporation or vapor permeation membranes has obvious advantages in the field of azeotropic separation. It can simplify the processes, save energy and reduce overall costs. It is also suitable for the separation of systems with low relative volatility. According to the relative position of



Fig. 15. 10 kt/a acetonitrile separation plant with the integration of distillation and molecular sieve membrane in Shandong Huihai Company.

the membrane and distillation column, five different coupling structures can be distinguished for membrane-assisted hybrid separations and the selective separation by means of membranes can also be exploited to remove reaction products and shift the chemical equilibrium, improving the reaction conversion. Common coupling structures include combinations of reactor-distillation-membrane and the coupling of reactive distillation with a membrane. Especially the inter-integration of reactive distillation with a membrane has been shown to have a significant effect on the performance. In addition, the integration of distillation and membrane is also commonly used to reduce production load for saving energy. Today many industrial applications of membrane-assisted distillation are known, specifically in the field of azeotrope separation.

Although a lot of progress, such as the preliminary molecular simulation of the membrane separation or the metaheuristics method used in the integration separation of simple mixtures, has been made on the integration of distillation and membrane separations, there are still two major issues with respect to process design worth continued research: (1) Establishing a precise molecular model of the membrane separation, which enables the prediction of the separation performance for different systems, promoting the research progress of membrane separation units. (2) Optimal design of the integrated distillation and membrane separation is still a challenge, as either specialized superstructure models need to be set up and solved, or robust simulation models need to be provided in order to apply metaheuristics, such as the response surface method or genetic algorithms to find the optimal integration and operating parameters.

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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.

Acknowledgments

This project has received funding from the National Key R&D Program of China (2019YFE0123200) and the Haihe Laboratory of Sustainable Chemical Transformations. The authors also thank the reviewers for their insightful comments and suggestions.

References

- [1] E.L. Cussler, B.K. Dutta, On separation efficiency, *AIChE J.* 58 (12) (2012) 3825–3831, <https://doi.org/10.1002/aic.13779>.
- [2] P.C. Wankat, Introduction to column distillation. *Separation Process Engineering, [M] Chapter 3*, 2007.
- [3] D.S. Sholl, R.P. Lively, Seven chemical separations to change the world, *Nature* 532 (7600) (2016) 435–437, <https://doi.org/10.1038/532435a>.
- [4] T.V. Gerven, A. Stankiewicz, Structure, energy, synergy, time—the fundamentals of process intensification, *Ind. Eng. Chem. Res.* 48 (5) (2009) 2465–2474, <https://doi.org/10.1021/ie801501y>.
- [5] M. Skiborowski, Process synthesis and design methods for process intensification, *Curr. Opin. Chem. Eng.* 22 (2018) 216–225, <https://doi.org/10.1016/j.coche.2018.11.004>.
- [6] C. Buchaly, P. Kreis, A. Gorak, Hybrid separation processes—combination of reactive distillation with membrane separation, *Chem. Eng. Process. -Process Intensif.* 46 (9) (2007) 790–799, <https://doi.org/10.1016/j.ccep.2007.05.023>.
- [7] W. Wang, Y. Wei, J. Fan, et al., Recent progress of two-dimensional nanosheet membranes and composite membranes for separation applications, *Front. Chem. Sci. Eng.* 15 (4) (2021) 793–819, <https://doi.org/10.1007/s11705-020-2016-8>.
- [8] S. Leaper, A. Abdel-Karim, P. Gorgojo, The use of carbon nanomaterials in membrane distillation membranes: a review, *Front. Chem. Sci. Eng.* 15 (4) (2021) 755–774, <https://doi.org/10.1007/s11705-020-1993-y>.
- [9] S. Hafeez, T. Safdar, E. Pallari, et al., CO₂ capture using membrane contactors: a systematic literature review, *Front. Chem. Sci. Eng.* 15 (4) (2021) 720–754, <https://doi.org/10.1007/s11705-020-1992-z>.
- [10] C.A. Scholes, Pilot plants of membrane technology in industry: challenges and key learnings, *Front. Chem. Sci. Eng.* 14 (3) (2020) 305–316, <https://doi.org/10.1007/s11705-019-1860-x>.
- [11] A.K. Tula, B. Befort, N. Garg, et al., Sustainable process design & analysis of hybrid separations, *Comput. Chem. Eng.* 105 (2017) 96–104, <https://doi.org/10.1016/j.compchemeng.2016.11.031>.
- [12] E. Bek-Pedersen, R. Gani, O. Levaux, Determination of optimal energy efficient separation schemes based on driving forces, *Comput. Chem. Eng.* 24 (2) (2000) 253–259, [https://doi.org/10.1016/S0098-1354\(00\)00474-9](https://doi.org/10.1016/S0098-1354(00)00474-9).
- [13] R.C. Binning, F.E. James, Permeation: a new way to separate mixtures, *Oil Gas J.* 56 (1958) 104–105.
- [14] F. Lipnizki, R.W. Field, P.K. Ten, Pervaporation-based hybrid process: a review of process design, applications and economics, *J. Membr. Sci.* 153 (2) (1999) 183–210, [https://doi.org/10.1016/S0376-7388\(98\)00253-1](https://doi.org/10.1016/S0376-7388(98)00253-1).
- [15] S. Sommer, T. Melin, Design and optimization of hybrid separation processes for the dehydration of 2-propanol and other organics, *Ind. Eng. Chem. Res.* 43 (17) (2004) 5248–5259, <https://doi.org/10.1021/ie034194d>.
- [16] L.M. Vane, F.R. Alvarez, Membrane-assisted vapor stripping: energy efficient hybrid distillation-vapor permeation process for alcohol-water separation, *J. Chem. Technol. Biotechnol.* 83 (9) (2008) 1275–1287, <https://doi.org/10.1002/jctb.1941>.
- [17] Y. Huang, R.W. Baker, L.M. Vane, Low-energy distillation-membrane separation process, *Ind. Eng. Chem. Res.* 49 (8) (2010) 3760–3768, <https://doi.org/10.1021/ie901545r>.
- [18] T. Yamaki, M. Yoshimune, N. Hara, et al., Heat-integrated hybrid membrane separation-distillation process for energy-efficient isopropyl alcohol dehydration, *J. Chem. Eng. Jpn.* 51 (10) (2018) 890–897, <https://doi.org/10.1252/jcej.18we039>.
- [19] W.-T. Han, Z.-W. Han, X.-C. Gao, et al., Inter-integration reactive distillation with vapor permeation for ethyl levulinate production: equipment development and experimental validating, *AIChE J.* (2021), e17441, <https://doi.org/10.1002/aic.17441>.
- [20] J.G. Wijmans, R.W. Baker, The solution-diffusion model: a review, *J. Membr. Sci.* 107 (1) (1995) 1–21, [https://doi.org/10.1016/0376-7388\(95\)00102-1](https://doi.org/10.1016/0376-7388(95)00102-1).
- [21] L.M. Vane, Review: membrane materials for the removal of water from industrial solvents by pervaporation and vapor permeation, *J. Chem. Technol. Biotechnol.* 94 (2) (2019) 343–365, <https://doi.org/10.1002/jctb.5839>.
- [22] R. Binning, R. Lee, J. Jennings, et al., Separation of liquid mixtures by permeation, *Ind. Eng. Chem.* 53 (1) (1961) 45–50.
- [23] R. Krishna, Describing the diffusion of guest molecules inside porous structures, *J. Phys. Chem. C* 113 (46) (2009) 19756–19781, <https://doi.org/10.1021/jp906879d>.
- [24] É. Csányi, T. Kristóf, G. Lendvay, Potential model development using quantum chemical information for molecular simulation of adsorption equilibria of water–methanol (ethanol) mixtures in zeolite NaA-4, *J. Phys. Chem. C* 113 (28) (2009) 12225–12235, <https://doi.org/10.1021/jp902520p>.
- [25] S. Guo, C. Yu, X. Gu, et al., Simulation of adsorption, diffusion, and permeability of water and ethanol in NaA zeolite membranes, *J. Membr. Sci.* 376 (1) (2011) 40–49, <https://doi.org/10.1016/j.memsci.2011.03.043>.
- [26] R. Krishna, J.M. van Baten, Diffusion of alkane mixtures in zeolites: validating the maxwell-stefan formulation using MD simulations, *J. Phys. Chem. B* 109 (13) (2005) 6386–6396, <https://doi.org/10.1021/jp0442571>.
- [27] R. Krishna, J.M. van Baten, Diffusion of hydrocarbon mixtures in MFI zeolite: influence of intersection blocking, *Chem. Eng. J.* 140 (1) (2008) 614–620, <https://doi.org/10.1016/j.ccej.2007.11.026>.
- [28] C. Zhang, L. Peng, J. Jiang, et al., Mass transfer model, preparation and applications of zeolite membranes for pervaporation dehydration: a review, *Chin. J. Chem. Eng.* 25 (11) (2017) 1627–1638, <https://doi.org/10.1016/j.cjche.2017.09.014>.
- [29] H. Shan, S. Li, X. Zhang, et al., Molecular dynamics simulation and preparation of vinyl modified polydimethylsiloxane membrane for pervaporation recovery of furfural, *Separ. Purif. Technol.* 258 (2021), 118006, <https://doi.org/10.1016/j.seppur.2020.118006>.
- [30] M. Berradi, O. Berradi, M. Chellouli, et al., Optimization of the synthesis of ultrafiltration asymmetric membranes based on organic polymers, *Res. Eng.* 6 (2020), <https://doi.org/10.1016/j.rineng.2020.100116>.
- [31] B. Scharzec, T. Waltermann, M. Skiborowski, A systematic approach towards synthesis and design of pervaporation-assisted separation processes, *Chem. Ing. Tech.* 89 (11) (2017) 1534–1549, <https://doi.org/10.1002/cite.201700079>.
- [32] Y. Wan, Y. Su, H. Zhou, Method for Separating Acetone-Butanol-Alcohol Fermenting Liquid by Utilizing Pervaporation-Rectification Coupling, *CN103772144A [P]*, 2014.
- [33] A. Norkobilov, D. Gorri, I. Ortiz, Process flowsheet analysis of pervaporation-based hybrid processes in the production of ethyl tert-butyl ether, *J. Chem. Technol. Biotechnol.* 92 (6) (2017) 1167–1177, <https://doi.org/10.1002/jctb.5186>.
- [34] Y. Zhu, Y. Huan, Z. Sun, et al., Device and Method for Recycling Ethyl Alcohol in Refined Mother Solution of Doxycycline Hyclate, *CN110294665A [P]*, 2019.
- [35] C. Yu, F. Xiangli, Y. Zhang, et al., Ethyl Alcohol Production Method and Device, *CN108083979A [P]*, 2018.
- [36] Z. Zhou, Industrial Equipment of Permeate Gas Ization Membrane and Rectifying Column Coupling Production Pure Alcohol, *CN206980472U [P]*, 2018.
- [37] W. Wu, H. Yu, L. Zhou, et al., Method for Refining Fuel Ethanol by Integrating Materials and Heat through Coupling Towers with Membrane, *CN110452092A [P]*, 2019.
- [38] Y. Zhang, J. Lu, W. Ji, et al., Method for Recovering and Purifying Ethanol-Ethyl Acetate-Piperazine Waste Solvent, *CN113527057A [P]*, 2021.
- [39] K. Sato, K. Aoki, K. Sugimoto, et al., Dehydrating performance of commercial LTA zeolite membranes and application to fuel grade bio-ethanol production by hybrid distillation/vapor permeation process, *Microporous Mesoporous Mater.* 115 (1–2) (2008) 184–188, <https://doi.org/10.1016/j.micromeso.2007.10.053>.
- [40] T. Roth, P. Kreis, A. Gorak, Process analysis and optimization of hybrid processes for the dehydration of ethanol, *Chem. Eng. Res. Des.* 91 (7) (2013) 1171–1185, <https://doi.org/10.1016/j.cherd.2013.01.016>.
- [41] D. Kunnakorn, T. Rirksomboon, K. Siemanond, et al., Techno-economic comparison of energy usage between azeotropic distillation and hybrid system for water-ethanol separation, *Renew. Energy* 51 (2013) 310–316, <https://doi.org/10.1016/j.renene.2012.09.055>.
- [42] J. Yang, M. Han, Optimization of distillation-pervaporation membrane hybrid process for separation of water/organic solvent mixtures, *Kor. Chem. Eng. Res.* 56 (1) (2018) 29–41, <https://doi.org/10.9713/kcer.2018.56.1.29>.
- [43] A. Tgarguifa, S. Abderafi, T. Bounahmidi, Energy efficiency improvement of a bioethanol distillery, by replacing a rectifying column with a pervaporation unit, *Renew. Energy* 122 (2018) 239–250, <https://doi.org/10.1016/j.renene.2018.01.112>.
- [44] F.J. Novita, H.-Y. Lee, M. Lee, Reactive distillation with pervaporation hybrid configuration for enhanced ethyl levulinate production, *Chem. Eng. Sci.* 190 (2018) 297–311, <https://doi.org/10.1016/j.ces.2018.06.024>.
- [45] C. Yu, H. Guo, Z. Ji, Economic feasibility analysis on application of zeolite membrane in bio-based fuel ethanol production, *Mod. Chem. Ind.* 39 (9) (2019) 192–194, <https://doi.org/10.16606/j.cnki.issn0253-4320.2019.09.041>.
- [46] H. Li, C. Guo, H. Guo, et al., Methodology for design of vapor permeation membrane-assisted distillation processes for aqueous azeotrope dehydration, *J. Membr. Sci.* 579 (2019) 318–328, <https://doi.org/10.1016/j.memsci.2019.03.009>.
- [47] X. Gao, S. Wang, J. Wang, et al., The study on the coupled process of column distillation and vapor permeation by NaA zeolite membrane for ethanol dehydration, *Chem. Eng. Res. Des.* 150 (2019) 246–253, <https://doi.org/10.1016/j.cherd.2019.08.003>.
- [48] J.C. Wang, J.Q. Zhang, Z. Hong, et al., A coupling process of distillation with vapor permeation and adsorption for production of fuel ethanol: a comparative analysis on energy consumption, *Ind. Eng. Chem. Res.* 61 (2) (2022) 1167–1178, <https://doi.org/10.1021/acs.iecr.1c01978>.
- [49] M.T.D.P. Gomez, A. Klein, J.-U. Repke, et al., A new energy-integrated pervaporation distillation approach, *Desalination* 224 (1) (2008) 28–33, <https://doi.org/10.1016/j.desal.2007.04.075>.
- [50] B. Scharzec, D. Merschhoff, J. Henrichs, et al., Evaluation of membrane-assisted hybrid processes for the separation of a tetrahydrofuran-methanol-water mixture, *Chem. Eng. Process. - Process Intensif.* 167 (2021), 108545, <https://doi.org/10.1016/j.ccep.2021.108545>.
- [51] F. Xiangli, W. Kong, Y. Zhang, et al., Technology and Device for Recovering Pyridine by Adopting Rectification-Vapor Permeation Coupling Method, *CN106117120A [P]*, 2016.
- [52] M. Matsukata, K. Kawazuishi, K. Mimura, et al., Method of Concentrating Water-Soluble Organic Substance Involves Distilling Raw Material Formed by the

- Mixture of Water-Soluble Organic Substance and Water and Performing Membrane Separation Process on Obtained Top Vapor, JP2013105620A [P], 2013.
- [53] B. Liu, H. Jin, W. Hou, et al., Separation Integration System and Separation Integration Method for Ethyl Acetate-Water System, CN106986769A [P], 2017.
- [54] E. Haaz, B. Szilagyi, D. Fozer, et al., Combining extractive heterogeneous-azeotropic distillation and hydrophilic pervaporation for enhanced separation of non-ideal ternary mixtures, *Front. Chem. Sci. Eng.* 14 (5) (2020) 913–927, <https://doi.org/10.1007/s11705-019-1877-1>.
- [55] V.V. Hoof, L.V.d. Abeele, A. Buekenhoudt, et al., Economic comparison between azeotropic distillation and different hybrid systems combining distillation with pervaporation for the dehydration of isopropanol, *Separ. Purif. Technol.* 37 (1) (2004) 33–49, <https://doi.org/10.1016/j.seppur.2003.08.003>.
- [56] A.J. Toth, Comprehensive evaluation and comparison of advanced separation methods on the separation of ethyl acetate-ethanol-water highly non-ideal mixture, *Separ. Purif. Technol.* 224 (2019) 490–508, <https://doi.org/10.1016/j.seppur.2019.05.051>.
- [57] B. Scharcz, D. Merschhoff, J. Henrichs, et al., Evaluation of membrane-assisted hybrid processes for the separation of a tetrahydrofuran-methanol-water mixture, *Chem. Eng. Process. - Process Intensif.* 167 (2021), 108545, <https://doi.org/10.1016/j.cep.2021.108545>.
- [58] M.T. Sanz, J. Gmehling, Study of the dehydration of isopropanol by a pervaporation-based hybrid process, *Chem. Eng. Technol.* 29 (4) (2006) 473–480, <https://doi.org/10.1002/ceat.200500340>.
- [59] P. Luis, A. Amelio, S. Vreysen, et al., Simulation and environmental evaluation of process design: distillation vs. hybrid distillation-pervaporation for methanol/tetrahydrofuran separation, *Appl. Energy* 113 (2014) 565–575, <https://doi.org/10.1016/j.apenergy.2013.06.040>.
- [60] B. Hassankhan, A. Raisi, Separation of isobutanol/water mixtures by hybrid distillation-pervaporation process: modeling, simulation and economic comparison, *Chem. Eng. Process. - Process Intensif.* 155 (2020), 108071, <https://doi.org/10.1016/j.cep.2020.108071>.
- [61] A. Andre, T. Nagy, A.J. Toth, et al., Distillation contra pervaporation: comprehensive investigation of isobutanol-water separation, *J. Clean. Prod.* 187 (2018) 804–818, <https://doi.org/10.1016/j.jclepro.2018.02.157>.
- [62] J. Holtbruegge, M. Wierschem, P. Lutze, Synthesis of dimethyl carbonate and propylene glycol in a membrane-assisted reactive distillation process: pilot-scale experiments, modeling and process analysis, *Chem. Eng. Process. - Process Intensif.* 84 (2014) 54–70, <https://doi.org/10.1016/j.cep.2014.01.008>.
- [63] M. Mihal, Z. Svandova, J. Markos, Steady state and dynamic simulation of a hybrid reactive separation process, *Chem. Pap.* 64 (2) (2010) 193–202, <https://doi.org/10.2478/s11696-009-0110-y>.
- [64] G.R. Harvianto, F. Ahmad, M. Lee, A hybrid reactive distillation process with high selectivity pervaporation for butyl acetate production via transesterification, *J. Membr. Sci.* 543 (2017) 49–57, <https://doi.org/10.1016/j.memsci.2017.08.041>.
- [65] H. Jin, J. Lu, J. Tang, et al., Simulation and analysis of a side stream reactive distillation-pervaporation integrated process for ethyl acetate production, *J. Chem. Ind. Eng.* 69 (8) (2018) 3469–3478, <https://doi.org/10.11949/j.issn.0438-1157.20180154>.
- [66] G.R. Harvianto, F. Ahmad, M. Lee, A thermally coupled reactive distillation and pervaporation hybrid process for n-butyl acetate production with enhanced energy efficiency, *Chem. Eng. Res. Des.* 124 (2017) 98–113, <https://doi.org/10.1016/j.cherd.2017.05.007>.
- [67] Y. Du, X. Ding, H. Wang, et al., Process for Separating Dimethyl Carbonate and Methanol by Employing Pervaporation and Pressure Distillation Integration, CN104370698A [P], 2015.
- [68] Y. Sun, Y. Huang, C. Yue, et al., Device and Process for Producing Propylene Glycol Monomethyl Ether Acetate by Reactive Distillation Coupled Pervaporation, CN112194580A [P], 2021.
- [69] M.T.D.P. Gomez, J.-U. Repke, D.-y. Kim, et al., Reduction of energy consumption in the process industry using a heat-integrated hybrid distillation pervaporation process, *Ind. Eng. Chem. Res.* 48 (9) (2009) 4484–4494, <https://doi.org/10.1021/ie801540a>.
- [70] H. Li, W. Li, D. Wu, Method for Recovering 2-methyl Tetrahydrofuran by Continuous Rectification and Steam Permeation, CN112159374A [P], 2021.
- [71] H. Zhou, Z. Zong, W. Jin, et al., Energy-saving Method for Performing Coupled Separation on an Organic Azeotropic System by Using a Distillation-Membrane Method, CN109745725A [P], 2019.
- [72] B. Sun, M. Wang, X. Meng, et al., Process and System for Recovering Absolute Ethyl Alcohol by Combining Rectification, Vaporizing Membrane and MVR Technology, CN112194567A [P], 2021.
- [73] M.T.D.P. Gomez, J.-U. Repke, D.-y. Kim, et al., Reduction of energy consumption in the process industry using a heat-integrated hybrid distillation pervaporation process, *Ind. Eng. Chem. Res.* 48 (9) (2009) 4484–4494, <https://doi.org/10.1021/ie801540a>.
- [74] H. Zhang, F. Zhao, Z. Ma, et al., Design and optimization for the separation of cyclohexane-isopropanol-water using mixed extractants with thermal integration based on molecular mechanism, *Separ. Purif. Technol.* 266 (2021), 118541, <https://doi.org/10.1016/j.seppur.2021.118541>.
- [75] Y. Wang, Z. Chen, Y. Shen, et al., Advanced exergy and exergoeconomic analysis of an integrated system combining CO₂ capture-storage and waste heat utilization processes, *Energy* 219 (2021), 119600, <https://doi.org/10.1016/j.energy.2020.119600>.
- [76] B. Shan, C. Niu, D. Meng, et al., Control of the azeotropic distillation process for separation of acetonitrile and water with and without heat integration, *Chem. Eng. Process. - Process Intensif.* 165 (2021), 108451, <https://doi.org/10.1016/j.cep.2021.108451>.
- [77] X. Li, X. Geng, P. Cui, et al., Thermodynamic efficiency enhancement of pressure-swilling distillation process via heat integration and heat pump technology, *Appl. Therm. Eng.* 154 (2019) 519–529, <https://doi.org/10.1016/j.applthermaleng.2019.03.118>.
- [78] F. Zhang, D. Sun, Y. Li, et al., Heat integration and dynamic control for separating the ternary azeotrope of butanone/isopropanol/n-heptane via pressure-swilling distillation, *Chem. Eng. Process. - Process Intensif.* 170 (2022), 108657, <https://doi.org/10.1016/j.cep.2021.108657>.
- [79] Z. Zhu, D. Xu, H. Jia, et al., Heat integration and control of a triple-column pressure-swilling distillation process, *Ind. Eng. Chem. Res.* 56 (8) (2017) 2150–2167, <https://doi.org/10.1021/acs.iecr.6b04118>.
- [80] P.C. Munasinghe, S.K. Khanal, Biomass-derived syngas fermentation into biofuels: opportunities and challenges, *Bioresour. Technol.* 101 (13) (2010) 5013–5022, <https://doi.org/10.1016/j.biortech.2009.12.098>.
- [81] D.X. Luo, Z.S. Hu, D.G. Choi, et al., Life cycle energy and greenhouse gas emissions for an ethanol production process based on blue-green algae, *Environ. Sci. Technol.* 44 (22) (2010) 8670–8677, <https://doi.org/10.1021/es1007577>.
- [82] H.N. Abubackar, M.C. Veiga, C. Kennes, Biological conversion of carbon monoxide: rich syngas or waste gases to bioethanol, *Biofuels Bioprod. & Bioref.* 5 (1) (2011) 93–114, <https://doi.org/10.1002/bbb.256>.
- [83] Y. Guan, S. Hu, Y. Wang, et al., Separating isopropanol from its diluted solutions via a process of integrating gas stripping and vapor permeation, *RSC Adv.* 5 (31) (2015) 24031–24037, <https://doi.org/10.1039/c5ra00879d>.
- [84] L.M. Vane, F.R. Alvarez, Hybrid vapor stripping-vapor permeation process for recovery and dehydration of 1-butanol and acetone/butanol/ethanol from dilute aqueous solutions. Part 1. Process simulations, *J. Chem. Technol. Biotechnol.* 88 (8) (2013) 1436–1447, <https://doi.org/10.1002/jctb.4087>.
- [85] L.M. Vane, F.R. Alvarez, Effect of membrane and process characteristics on cost and energy usage for separating alcohol-water mixtures using a hybrid vapor stripping-vapor permeation process, *J. Chem. Technol. Biotechnol.* 90 (8) (2015) 1380–1390, <https://doi.org/10.1002/jctb.4695>.
- [86] L.M. Vane, F.R. Alvarez, Y. Huang, et al., Experimental validation of hybrid distillation-vapor permeation process for energy efficient ethanol-water separation, *J. Chem. Technol. Biotechnol.* 85 (4) (2010) 502–511, <https://doi.org/10.1002/jctb.2318>.
- [87] L.M. Vane, F.R. Alvarez, L. Rosenblum, et al., Efficient ethanol recovery from yeast fermentation broth with integrated distillation-membrane process, *Ind. Eng. Chem. Res.* 52 (3) (2013) 1033–1041, <https://doi.org/10.1021/ie2024917>.
- [88] L.M. Vane, F.R. Alvarez, L. Rosenblum, et al., Hybrid vapor stripping-vapor permeation process for recovery and dehydration of 1-butanol and acetone/butanol/ethanol from dilute aqueous solutions. Part 2. Experimental validation with simple mixtures and actual fermentation broth, *J. Chem. Technol. Biotechnol.* 88 (8) (2013) 1448–1458, <https://doi.org/10.1002/jctb.4086>.
- [89] L. Zhou, H. Yu, Y. Pan, et al., Three-column Two-Membrane Coupled Reinforced Refining Method for Fuel Ethanol, CN110483248A [P], 2019.
- [90] H. Kuhlmann, M. Skiborowski, Optimization-based approach to process synthesis for process intensification: general approach and application to ethanol dehydration, *Ind. Eng. Chem. Res.* 56 (45) (2017) 13461–13481, <https://doi.org/10.1021/acs.iecr.7b02226>.
- [91] K. Gudena, G.P. Rangaiah, S. Lakshminarayanan, HiGee stripper-membrane system for decentralized bioethanol recovery and purification, *Ind. Eng. Chem. Res.* 52 (12) (2013) 4572–4585, <https://doi.org/10.1021/ie302557f>.
- [92] M. Skiborowski, J. Wessel, W. Marquardt, Efficient optimization-based design of membrane-assisted distillation processes, *Ind. Eng. Chem. Res.* 53 (40) (2014) 15698–15717, <https://doi.org/10.1021/ie502482b>.
- [93] M. Skiborowski, A. Harwardt, W. Marquardt, Conceptual design of distillation-based hybrid separation processes, *Ann. Rev. Chem. Biomol. Eng.* 4 (2013) 45–68, <https://doi.org/10.1146/annurev-chembioeng-061010-114129>.
- [94] W. Xiao, Y. Zhou, X. Ruan, et al., Parameters optimisation of isopropanol purification by hybrid distillation-vapour permeation process using response surface methodology, *Chem. Eng. Transact.* 45 (2015) 1171–1176, <https://doi.org/10.3303/CET1545196>.
- [95] G.R. Harvianto, F. Ahmad, N. Le Cao, et al., Vapor permeation-distillation hybrid processes for cost-effective isopropanol dehydration: modeling, simulation and optimization, *J. Membr. Sci.* 497 (2016) 108–119, <https://doi.org/10.1016/j.memsci.2015.09.032>.
- [96] V.N. Kiva, E.K. Hilmen, S. Skogestad, Azeotropic phase equilibrium diagrams: a survey, *Chem. Eng. Sci.* 58 (10) (2003) 1903–1953, [https://doi.org/10.1016/S0009-2509\(03\)00018-6](https://doi.org/10.1016/S0009-2509(03)00018-6).
- [97] B. Szilagyi, T.D.T. Huyen, D. Fozer, et al., Modelling of hybrid method for VOC removal from process wastewater: distillation and hydrophilic pervaporation, *Period. Polytech. - Chem. Eng.* 64 (3) (2020) 364–370, <https://doi.org/10.3311/PPch.15190>.
- [98] J. Lv, Y. Li, S. Mei, et al., Separation Method of Ethylenediamine and Water Azeotrope, CN103539675A [P], 2014.
- [99] C. Servel, E. Favre, D. Roizard, Possibilities and limitations of pervaporation for improved acetic acid dehydration by distillation at industrial scale: a critical analysis, *Procedia Eng.* 44 (2012) 2065–2067, <https://doi.org/10.1016/j.proeng.2012.09.047>.
- [100] Z. Zhou, Industrial Device for Producing High-Purity Ethylene Glycol Dimethyl Ether through Membrane-Column Coupling, CN107162881A [P], 2017.
- [101] Z. Tu, J. Xia, Y. Sun, et al., Study on the process design of pervaporation dehydrate for acetonitrile waste, *Acta Sci. Nat. Universitatis Nankaiensis* 47 (6) (2014) 53–58.

- [102] S. Steinigeweg, J. Gmehling, Transesterification processes by combination of reactive distillation and pervaporation, *Chem. Eng. Process. - Process Intensif.* 43 (3) (2004) 447–456, [https://doi.org/10.1016/s0255-2701\(03\)00129-6](https://doi.org/10.1016/s0255-2701(03)00129-6).
- [103] K. Koczka, P. Mizsey, Z. Fonyo, Rigorous modelling and optimization of hybrid separation processes based on pervaporation, *Cent. Eur. J. Chem.* 5 (4) (2007) 1124–1147, <https://doi.org/10.2478/s11532-007-0050-8>.
- [104] P. Pribic, M. Roza, L. Zuber, How to improve the energy savings in distillation and hybrid distillation-pervaporation systems, *Separ. Sci. Technol.* 41 (11) (2006) 2581–2602, <https://doi.org/10.1080/01496390600745685>.
- [105] C. Zong, Q. Guo, B. Shen, et al., Heat-integrated pervaporation-distillation hybrid system for the separation of methyl acetate-methanol azeotropes, *Ind. Eng. Chem. Res.* 60 (28) (2021) 10327–10337, <https://doi.org/10.1021/acs.iecr.1c01513>.
- [106] A. Gorak, A. Hoffmann, P. Kreis, Processes intensification: reactive and membrane supported rectification, *Chem. Ing. Tech.* 79 (10) (2007) 1581–1600, <https://doi.org/10.1002/cite.200700111>.
- [107] P. Kreis, A. Gorak, Process analysis of hybrid separation processes - combination of distillation and pervaporation, *Chem. Eng. Res. Des.* 84 (A7) (2006) 595–600, <https://doi.org/10.1205/cherd.05211>.
- [108] P. Kreis, A. Gorak, Modelling and Simulation of a Combined Membrane/Distillation Process, 13th European Symposium on Computer Aided Process Engineering (ESCAPE-13), Lappeenranta, Finland, 2003, pp. 743–748.
- [109] A. Norkobilov, D. Gorri, I. Ortiz, Comparative study of conventional, reactive-distillation and pervaporation integrated hybrid process for ethyl tert-butyl ether production, *Chem. Eng. Process. - Process Intensif.* 122 (2017) 434–446, <https://doi.org/10.1016/j.cep.2017.07.003>.
- [110] A. Singh, G.P. Rangaiah, Development and optimization of a novel process of double-effect distillation with vapor recompression for bioethanol recovery and vapor permeation for bioethanol dehydration, *J. Chem. Technol. Biotechnol.* 94 (4) (2019) 1041–1056, <https://doi.org/10.1002/jctb.5851>.
- [111] O. Babaie, M.N. Esfahany, The hybrid RDWC-pervaporation with series-parallel arrangement and heat integration for ETBE production, *Separ. Purif. Technol.* 268 (2021), 118695, <https://doi.org/10.1016/j.seppur.2021.118695>.
- [112] O. Babaie, M.N. Esfahany, Optimum process configuration for ETBE production based on TAC minimization, *Separ. Purif. Technol.* 256 (2021), 117744, <https://doi.org/10.1016/j.seppur.2020.117744>.
- [113] T.G. Pressly, K.M. Ng, A break-even analysis of distillation-membrane hybrids, *AIChE J.* 44 (1) (1998) 93–105, <https://doi.org/10.1002/aic.690440111>.
- [114] R. Zarca, A. Ortiz, D. Gorri, et al., Optimized distillation coupled with state-of-the-art membranes for propylene purification, *J. Membr. Sci.* 556 (2018) 321–328, <https://doi.org/10.1016/j.memsci.2018.04.016>.
- [115] J. Ploegmakers, A.R.T. Jelsma, A.G.J. van der Ham, et al., Economic evaluation of membrane potential for ethylene/ethane separation in a retrofitted hybrid membrane-distillation plant using unisim design, *Ind. Eng. Chem. Res.* 52 (19) (2013) 6524–6539, <https://doi.org/10.1021/ie400737s>.
- [116] J. Park, K. Kim, J.-W. Shin, et al., Performance study of multistage membrane and hybrid distillation processes for propylene/propane separation, *Can. J. Chem. Eng.* 95 (12) (2017) 2390–2397, <https://doi.org/10.1002/cjce.22914>.
- [117] J.A. Caballero, I.E. Grossmann, M. Keyvani, et al., Design of hybrid distillation-vapor membrane separation systems, *Ind. Eng. Chem. Res.* 48 (20) (2009) 9151–9162, <https://doi.org/10.1021/ie900499y>.
- [118] Y. Naidu, R.K. Malik, A generalized methodology for optimal configurations of hybrid distillation-pervaporation processes, *Chem. Eng. Res. Des.* 89 (8A) (2011) 1348–1361, <https://doi.org/10.1016/j.cherd.2011.02.025>.
- [119] Q. Liu, Y. Su, H. Gao, Separation of acetic acid/water mixture by distillation and distillation coupled pervaporation, *Comput. Appl. Chem.* 19 (3) (2002) 211–214, <https://doi.org/10.16866/j.com.app.chem.2002.03.004>.
- [120] J. Park, S.-J. Kim, I. Lee, et al., Techno-economics and sensitivity analysis of hybrid process combining carbon molecular sieve membrane and distillation column for propylene/propane separation, *Chem. Eng. Res. Des.* 172 (2021) 204–214, <https://doi.org/10.1016/j.cherd.2021.06.009>.
- [121] J. Fontalvo, J.T.F. Kerurentjes, A hybrid distillation-pervaporation system in a single unit for breaking distillation boundaries in multicomponent mixtures, *Chem. Eng. Res. Des.* 99 (2015) 158–164, <https://doi.org/10.1016/j.cherd.2015.02.019>.
- [122] A.I. Stankiewicz, J.A. Moulijn, Process intensification: transforming chemical engineering, *Chem. Eng. Prog.* 96 (2) (2000) 22–34.
- [123] J.A. Leon, B. Schuur, J. Fontalvo, Hybrid distillation-pervaporation in a single unit: experimental proof of concept in a batch operation, *Separ. Purif. Technol.* 252 (2020), 117464, <https://doi.org/10.1016/j.seppur.2020.117464>.
- [124] J.A. Leon, J. Fontalvo, Theoretical and experimental evaluation of a distillation-pervaporation in a single unit column for the separation of an azeotropic mixture, *Ind. Eng. Chem. Res.* 59 (43) (2020) 19426–19437, <https://doi.org/10.1021/acs.iecr.0c03885>.
- [125] J.A. Leon, J. Fontalvo, Conceptual design of distillation-pervaporation in single unit columns using residue curve map methodology, *Chem. Eng. Process. - Process Intensif.* 153 (2020), 107966, <https://doi.org/10.1016/j.cep.2020.107966>.
- [126] J.A. Leon, J. Fontalvo, Analysis of a hybrid distillation-pervaporation column in a single unit: intermediate membrane section in the rectifying and stripping section, *Can. J. Chem. Eng.* 98 (10) (2020) 2227–2237, <https://doi.org/10.1002/cjce.23765>.
- [127] J.B. Haelssig, A.Y. Tremblay, J. Thibault, A new hybrid membrane separation process for enhanced ethanol recovery: process description and numerical studies, *Chem. Eng. Sci.* 68 (1) (2012) 492–505, <https://doi.org/10.1016/j.ces.2011.10.012>.
- [128] J.B. Haelssig, J. Thibault, A.Y. Tremblay, Numerical investigation of membrane dephlegmation: a hybrid pervaporation-distillation process for ethanol recovery, *Chem. Eng. Process. - Process Intensif.* 50 (11–12) (2011) 1226–1236, <https://doi.org/10.1016/j.cep.2011.08.003>.
- [129] J.A. Leon, J. Fontalvo, Tools for the design of hybrid distillation-pervaporation columns in a single unit: hybrid rectifying-pervaporation section, *Ind. Eng. Chem. Res.* 57 (35) (2018) 11970–11980, <https://doi.org/10.1021/acs.iecr.8b02078>.
- [130] A. Boontawan, Purification of succinic acid from synthetic solution using vapor permeation-assisted esterification coupled with reactive distillation, *Adv. Mater. Res.* 550–553 (2012) 3008–3011, <https://doi.org/10.4028/www.scientific.net/AMR.550-553.3008>.
- [131] X. Gu, Z. Qing, C. Yu, et al., Method and Device for Producing Diethyl Maleate by Rectification and Steam Osmosis Coupling, CN104262140A [P], 2015.
- [132] H. Wu, M. Jiang, W. Jin, et al., Process for Separating Acetone, Butanol, and Ethanol in Situ by Coupling Biomass Fermentation and Pervaporation, CN101805754A [P], 2010.
- [133] Q. Hu, Y. Li, J. Xie, et al., Energy-saving Production Process and Apparatus of Ethyl Lactate, CN109438228A [P], 2019.
- [134] I. Aguirre, M.B. Gueemez, A. Motelica, et al., A techno-economic comparison of various process options for the production of 1,1-diethoxy butane, *J. Chem. Technol. Biotechnol.* 87 (7) (2012) 943–954, <https://doi.org/10.1002/jctb.3704>.
- [135] H.J. Wang, B.L. Yang, J. Wu, et al., Multi-fields synergy in the process of reactive distillation coupled with membrane separation, *Chem. Eng. Process. - Process Intensif.* 44 (11) (2005) 1207–1215, <https://doi.org/10.1016/j.cep.2005.03.007>.
- [136] B. Lv, G. Liu, X. Dong, et al., Novel reactive distillation-pervaporation coupled process for ethyl acetate production with water removal from reboiler and acetic acid recycle, *Ind. Eng. Chem. Res.* 51 (23) (2012) 8079–8086, <https://doi.org/10.1021/ie3004072>.
- [137] A. Arpornwichanop, U. Sahapatsombud, Y. Patcharavorachot, et al., Hybrid process of reactive distillation and pervaporation for the production of tert-amyl ethyl ether, *Chin. J. Chem. Eng.* 16 (1) (2008) 100–103, [https://doi.org/10.1016/s1004-9541\(08\)60045-2](https://doi.org/10.1016/s1004-9541(08)60045-2).
- [138] J. Tang, X. Qiao, H. Jin, et al., Method and Device for Integrated Production of Ethyl Acetate through Reactive Distillation and Penetration Vaporization, CN108059597A [P], 2018.
- [139] F. Aiouache, S. Goto, Reactive distillation-pervaporation hybrid column for tert-amyl alcohol etherification with ethanol, *Chem. Eng. Sci.* 58 (12) (2003) 2465–2477, [https://doi.org/10.1016/s0009-2509\(03\)00116-7](https://doi.org/10.1016/s0009-2509(03)00116-7).
- [140] X. Gao, W. Han, H. Li, et al., In-tower Reactive Rectification and Membrane Coupling Method and Device, CN112250574A [P], 2021.
- [141] K. Wu, H. Li, X. Li, et al., Inter-integration reactive distillation with vapor permeation for ethyl levulinate production: modeling, process analysis and design, *Chem. Eng. Sci.* 245 (2021), 116962, <https://doi.org/10.1016/j.ces.2021.116962>.
- [142] X. Ding, C. Wang, R. Tu, et al., Device and Process for Preparing Methanol and Butyl Acetate, CN110743372A [P], 2020.
- [143] G. Li, C. Wang, C. Guang, et al., Energy-saving investigation of hybrid reactive distillation for n-butyl acetate production from two blending feedstocks, *Separ. Purif. Technol.* 235 (2020), 116163, <https://doi.org/10.1016/j.seppur.2019.116163>.
- [144] L. Zhang, X. Zhao, Z. Zhao, et al., Tetrahydrofuran Dewatering Process Coupling Pervaporation Membrane with Pressure-Swing Distillation, CN106543112A [P], 2017.
- [145] H. Zhang, S. Wang, J. Tang, et al., Multi-objective optimization and control strategy for extractive distillation with dividing-wall column/pervaporation for separation of ternary azeotropes based on mechanism analysis, *Energy* 229 (2021), 120774, <https://doi.org/10.1016/j.energy.2021.120774>.
- [146] Y. Wu, D. Meng, D. Yao, et al., Mechanism analysis, economic optimization, and environmental assessment of hybrid extractive distillation-pervaporation processes for dehydration of n-propanol, *ACS Sustain. Chem. Eng.* 8 (11) (2020) 4561–4571, <https://doi.org/10.1021/acssuschemeng.0c00263>.
- [147] L.S. White, Development of large-scale applications in organic solvent nanofiltration and pervaporation for chemical and refining processes, *J. Membr. Sci.* 286 (1–2) (2006) 26–35, <https://doi.org/10.1016/j.memsci.2006.09.006>.
- [148] C. Wang, Z. Zhang, X. Zhang, et al., Energy-saving hybrid processes combining pressure-swing reactive distillation and pervaporation membrane for n-propyl acetate production, *Separ. Purif. Technol.* 221 (2019) 1–11, <https://doi.org/10.1016/j.seppur.2019.03.074>.
- [149] C. Wang, C. Wang, C. Guang, et al., Hybrid reactive distillation using polyoctylmethylsiloxane membrane for isopentyl acetate production from mixed PVA by products, *J. Chem. Technol. Biotechnol.* 94 (2) (2019) 527–537, <https://doi.org/10.1002/jctb.5799>.
- [150] S. van Wyk, A.G.J. van der Ham, S.R.A. Kersten, Pervaporative separation and intensification of downstream recovery of acetone-butanol-ethanol (ABE), *Chem. Eng. Process. - Process Intensif.* 130 (2018) 148–159, <https://doi.org/10.1016/j.cep.2018.06.011>.
- [151] A. Rom, A. Miltner, W. Wukovits, et al., Energy saving potential of hybrid membrane and distillation process in butanol purification: experiments, modelling and simulation, *Chem. Eng. Process. - Process Intensif.* 104 (2016) 201–211, <https://doi.org/10.1016/j.cep.2016.03.012>.
- [152] W. Osorio-Viana, H.N. Ibarra-Taquez, I. Dobrosz-Gomez, et al., Hybrid membrane and conventional processes comparison for isoamyl acetate production, *Chem. Eng. Process. - Process Intensif.* 76 (2014) 70–82, <https://doi.org/10.1016/j.cep.2013.12.005>.
- [153] F.J. Novita, H.-Y. Lee, M. Lee, Energy-efficient and ecologically friendly hybrid extractive distillation using a pervaporation system for azeotropic feed

- compositions in alcohol dehydration process, *J. Taiwan Inst. Chem. Eng.* 91 (2018) 251–265, <https://doi.org/10.1016/j.jtice.2018.05.023>.
- [154] Q. Li, A.A. Kiss, Novel pervaporation-assisted pressure swing reactive distillation process for intensified synthesis of dimethyl carbonate, *Chem. Eng. Process. - Process Intensif.* 162 (2021), 108358, <https://doi.org/10.1016/j.cep.2021.108358>.
- [155] L. Li, S. Chai, L. Liu, et al., Study on separation of mixed alcohol from water phase by-product in the F-T synthesis by pervaporation technology, *Chem. Ind. Eng. Prog.* 36 (6) (2017) 2086–2093, <https://doi.org/10.16085/j.issn.1000-6613.2017.06.017>.
- [156] H.-Y. Lee, S.-Y. Li, C.-L. Chen, Evolutional design and control of the equilibrium-limited ethyl acetate process via reactive distillation-pervaporation hybrid configuration, *Ind. Eng. Chem. Res.* 55 (32) (2016) 8802–8817, <https://doi.org/10.1021/acs.iecr.6b01358>.
- [157] A. Khazaei, V. Mohebbi, R.M. Behbahani, et al., Energy consumption in pervaporation, conventional and hybrid processes to separate toluene and i-octane, *Chem. Eng. Process. - Process Intensif.* 128 (2018) 46–52, <https://doi.org/10.1016/j.cep.2018.04.009>.
- [158] G. Genduso, A. Amelio, E. Colombini, et al., Retrofitting of extractive distillation columns with high flux, low separation factor membranes: a way to reduce the energy demand? *Chem. Eng. Res. Des.* 109 (2016) 127–140, <https://doi.org/10.1016/j.cherd.2016.01.013>.
- [159] Y. Dai, S. Li, D. Meng, et al., Economic and environmental evaluation for purification of diisopropyl ether and isopropyl alcohol via combining distillation and pervaporation membrane, *ACS Sustain. Chem. Eng.* 7 (24) (2019) 20170–20179, <https://doi.org/10.1021/acssuschemeng.9b06198>.
- [160] P. Cui, F. Zhao, X. Liu, et al., Sustainable wastewater treatment via PV-distillation hybrid process for the separation of ethyl acetate/isopropanol/water, *Separ. Purif. Technol.* 257 (2021), 117919, <https://doi.org/10.1016/j.seppur.2020.117919>.
- [161] D. Cai, H. Chen, C. Chen, et al., Gas stripping-pervaporation hybrid process for energy-saving product recovery from acetone-butanol-ethanol (ABE) fermentation broth, *Chem. Eng. J.* 287 (2016) 1–10, <https://doi.org/10.1016/j.cej.2015.11.024>.
- [162] P.N. Ashani, M. Shafiei, K. Karimi, Biobutanol production from municipal solid waste: technical and economic analysis, *Bioresour. Technol.* 308 (2020), 123267, <https://doi.org/10.1016/j.biortech.2020.123267>.
- [163] H.G. Kim, H.R. Na, H.R. Lee, et al., Distillation-pervaporation membrane hybrid system for epichlorohydrin and isopropyl alcohol recovery in epoxy resin production process, *Separ. Purif. Technol.* 254 (2021) 10, <https://doi.org/10.1016/j.seppur.2020.117678>.
- [164] Z. Huang, Y. Lin, X. Wang, et al., Optimization and control of a reactive distillation process for the synthesis of dimethyl carbonate, *Chin. J. Chem. Eng.* 25 (8) (2017) 1079–1090, <https://doi.org/10.1016/j.cjche.2017.03.039>.
- [165] Z.-Y. Hu, H.-B. Li, Y.-X. Tan, et al., Zeolite membrane dehydration and distillation coupling process simulation of F-T water by-product recovery, *Chem. Ind. Eng. Prog.* 35 (2016) 56–60, <https://doi.org/10.16085/j.issn.1000-6613.2016.s2.009>.