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APPLICATION OF MEMBRANE PROCESSES IN THE DEHYDRATION OF BIOETHANOL

Highlights

- Membrane processes have been proposed as alternatives to distillation and adsorption
- Pervaporation and vapour permeation are applied in ethanol dehydration systems
- Hydrophilic membranes increase ethanol purity from 96 to over 99 vol.%
- A comparative study examines organic, inorganic, and composite membranes
- Membrane-based separations offer energy-efficient bioethanol purification

Abstract

Bioethanol is an extremely important raw material on the world market that is used in various industries. The purification processes most commonly used in modern biorefineries include distillation for ethanol extraction, followed by zeolite adsorption for bioethanol dehydration. Both processes are very energy-intensive. Membrane separation processes have significant potential to replace both steps in bioethanol production, which could significantly lower operating costs and reduce production costs. This paper describes the implementation of pervaporation and vapour permeation in the bioethanol dehydration process. The aim is to increase the ethanol concentration from 96% vol. at the outlet of the distillation column to over 99% vol. by using hydrophilic membranes that are able to selectively pass water molecules and thus remove them from the bioethanol. Based on the existing literature, the study determines the optimal process parameters such as temperature, pressure, flow rate, and pressure on the permeate side. Furthermore, the performance of different organic, inorganic, and composite membranes is presented, and the maintenance of these parameters, as well as the decreasing performance of the materials during prolonged use, is discussed.

Keywords: pervaporation, vapour permeation, zeolite membranes, composite membranes, polymeric materials.

REVIEW PAPER

UDC

INTRODUCTION

As awareness of the need to preserve the planet has grown worldwide, new technologies have emerged that aim to minimise man's impact on the environment. One particularly interesting idea is to partially replace fossil fuels with bioethanol in order to reduce carbon dioxide emissions and thus mitigate the greenhouse effect, which is thought to contribute to global warming. However, a major challenge with this approach is that maize, the most commonly used raw material for bioethanol production, is also a staple food for humans and livestock. This raises concerns among researchers that food prices could rise in the future because maize is used as both a biofuel and a food source. Given the high production costs of bioethanol, it is currently unrealistic to expect that fossil fuels can be replaced by ethanol as an energy source in the near future [1].

Biorefineries in the broadest sense are plants that process biomass to produce a wide range of market-relevant products, including biofuels. While ethanol production has been around for some time, the concept of refining biomass to produce other biotechnological products on an industrial scale only emerged in the 1980s. During this time, processes were developed to produce products similar to those from conventional refineries, the main difference being that the primary feedstock is biomass rather than crude oil [2].

Biorefineries are often categorised into first-, second-, and third-generation biorefineries according to the type of raw materials used. First-generation biorefineries use

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plants such as maize, sugar beet, or sugar cane as feedstock. Second-generation biorefineries rely on organic residues from industry or forestry, while third-generation biorefineries use microalgae or cyanobacteria as biomass sources. Although second- and third-generation biorefineries offer the greatest potential for environmental sustain-ability, the technology is currently neither cost-effective nor widespread enough to dominate the market [2].

The most energy-intensive steps in conventional bioethanol production are distillation and dehydration. Membrane separation processes have emerged as a promising alternative, with pervaporation (PV) and vapour permeation (VP) being the most commonly used membrane-based processes for bioethanol drying [1]. Pervaporation is a particularly interesting, sustainable, and highly efficient membrane technology that provides high cost and energy savings, environmental safety, and scalability. A key strength of PV lies in its ability to selectively remove water during the dehydration of alcohol and solvent mixtures [3,4].

The production of bioethanol in a biorefinery

First-generation biorefineries are currently the most widely used processes for the production of bioethanol. Figure 1 shows a simplified diagram of the bioethanol production process using maize as the main raw material.

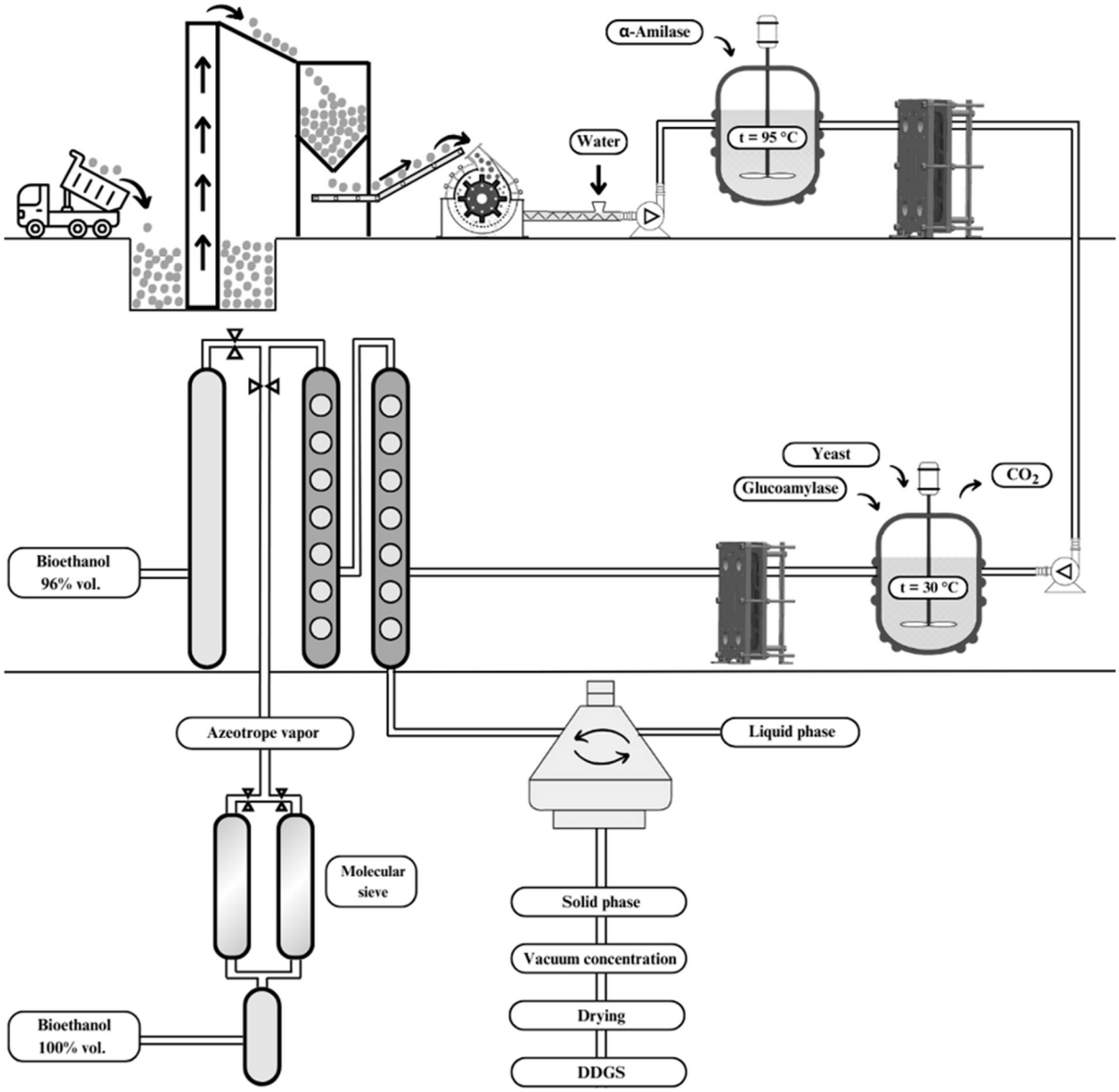

Figure 1. Schematic of the bioethanol production process.

In a biorefinery, the maize is delivered by lorry and unloaded into underground storage bunkers. From there, it is transported by an elevator to the storage silos. The maize is then transported by belt or chain conveyors to a hammer mill, where it is ground into coarse flour. The crushed maize is mixed with hot water in a screw conveyor and transported to a bioreactor, where a thermostable enzyme, α-amylase, is added. This enzyme breaks down the starch (a poly-saccharide) at relatively high temperatures into fractions with a lower molecular weight, which are known as dextrins

(oligosaccharides). The starch initially gelatinises and forms a highly viscous mass. The task of α-amylase is to liquefy the starch so that the resulting mixture can be pumped through heat exchangers [5,6].

After liquefaction, the mixture is cooled from 95 °C to 30 °C in a plate heat exchanger before being sent to the next bioreactor for fermentation. In bioethanol production from maize, the optimum temperature range for fermentation is between 25 °C and 35 °C to maximise ethanol yield. Temperatures that are too low can slow down or prevent fermentation altogether, while temperatures that are too high can have a negative impact on ethanol yield [6].

The material entering the bioreactor contains a significant amount of dextrins that cannot be metabolised by the yeast. To convert these dextrins into fermentable sugars (mono-, di-, and trisaccharides), the enzyme glucoamylase is introduced into the reactor. The dosage of this enzyme is carefully controlled to prevent a sudden accumulation of simple sugars, which would increase the osmotic pressure in the system. This stress could cause the yeast to produce an excessive amount of glycerol, which would reduce the ethanol yield. Since saccharification of dextrin by glucoamylase and alcoholic fermentation by yeast occur simultaneously, this process is often referred to as simultaneous saccharification and fermentation [6].

After fermentation, the resulting mixture contains about 10–15% ethanol, 80–85% water, and 5–10% dry matter, as well as small amounts of volatile compounds that can significantly influence the sensory properties of bioethanol. The entire fermented mixture is first heated in a plate heat exchanger before being fed into a distillation column (the first column), where ethanol is extracted from the mixture by direct contact with superheated vapour. On one side of the distillation column, the spent fermentation mixture is drawn off and separated into a solid and a liquid phase by centrifugation. The solid phase is concentrated in a vacuum evaporator, dried in a dryer, packaged, and sold as animal feed (DDGS – Dried Distillers Grains with Solubles). On the other hand, the ethanol–water vapours with other volatile impurities leave the distillation column and enter the rectification column (the second column). The main objective here is to concentrate the bioethanol to 96% vol. through multi-stage distillation and, at the same time, remove unwanted impurities which, even in trace amounts, can significantly affect the quality and market value of the bioethanol. The rectification column consists of several trays arranged in such a way that ascending vapours can interact with descending distillate liquid (reflux). Each tray functions as a miniature distillation unit, which is why rectification is considered a multi-stage distillation process [5,6].

At the exit of the rectification column, the resulting azeotropic vapour mixture contains 96% ethanol by volume, while the rest is mainly water. This mixture can either be condensed to obtain bioethanol with a concentration of 96% vol. or passed through molecular sieves that adsorb the remaining water to achieve a final ethanol concentration above 99% vol. The columns with molecular sieves are filled with zeolite particles, which, due to their high porosity and large surface area, efficiently adsorb water while allowing ethanol molecules to pass through. Over time, the zeolites become saturated and lose their ability to bind water. To restore their functionality, a desorption process is carried out to remove the water. As continuous bioethanol production is the aim, at least two zeolite columns are usually installed – one working while the other is regenerated [6].

Membrane technology for the dehydration of bioethanol

Pervaporation and vapour permeation are membrane separation processes driven by a gradient of partial pressures across a selective membrane. In PV, components selectively sorb into the membrane, diffuse through it, and evaporate on the permeate side, which is maintained under vacuum or swept with an inert gas. The processes of PV and VP are almost identical. The only difference is that the starting solution in PV is in a liquid state, whereas in vapour permeation, it is in a gaseous state. The separation mechanism (sorption–diffusion) is similar, but in VP, no phase change occurs at the membrane interface because the feed is already vaporised [7,8]. In both processes, a hydrophilic membrane is used, whereby the permeate is in the vapour phase and consists mainly of water (Table 1).

The overall efficiency of the PV process is heavily dependent on the membrane material. This creates a strong need for the continuous development of novel membranes with enhanced selectivity and transport properties [9].

Membranes for bioethanol dehydration

The same membrane materials can be used for PV and vapour permeation, as both ethanol dehydration processes require a hydrophilic membrane that allows the water to pass through as permeate via the solution–diffusion mechanism, while the ethanol, which has no affinity for such a membrane, remains in the retentate [10]. The main difference between these two processes lies in the operating conditions, namely the aggregate state of the feed solution, which has a direct impact on the design of the separation system. In both processes, the driving force is the gradient of partial pressures across the membrane. Due to the incompressibility of the feed solution, high pressure is not required for PV, which means that the membranes for PV do not need to be particularly resistant to high pressures. For vapour permeation, due to the compressibility of the feed solution and the need for relatively high pressures, the membranes must be resistant to high pressures and high temperatures, which are much higher for vapour permeation than for PV [1,11].

The characteristics of a good membrane include a sharp separation, a high flux rate with the lowest possible driving force, and good thermal, chemical, mechanical, and microbiological stability [12]. Membranes can be made from both organic and inorganic materials, and these materials are often combined. An example of this is the impregnation of organic polymer membranes with nanoparticles of inorganic origin [2].

Table 1. Fundamental properties of membrane processes in the dehydration of bioethanol.

Process	Feed	Permeate	Membrane	Transport mechanism
Pervaporation	Liquid	Gas	Hydrophilic	Solution–diffusion
Vapor permeation	Gas	Gas	Hydrophilic	Solution–diffusion

Organic polymers can be of natural or synthetic origin. Synthetic organic polymers are among the predominant materials used in the production of membranes, especially due to the extensive possibilities for macromolecular cross-linking, which makes it very easy to improve mechanical stability as well as adequate separation capacity at very low cost [13]. Polymeric membranes are generally cheaper than inorganic membranes, but they have lower flux and selectivity. They are also limited in thermal stability, with temperature limits around 100 °C [14]. Commonly used polymers include polyvinyl alcohol (PVA), chitosan (CS), alginate (Alg), polyamide (PA), polyimide (PI), polyacrylonitrile (PAN), polyelectrolyte (PE), polyaniline (PANI), polyurea (PU), and polysulfone (PSF) [4]. The disadvantages of polymer membranes include very low resistance to swelling, poor chemical and thermal stability, and the difficulty of reconciling sufficiently high permeability with adequate selectivity [15]. Swelling is a significant limitation in PV membranes, particularly during the separation of organic-organic or organic-water mixtures, where strong sorption of penetrant molecules can cause physical expansion of the polymer matrix [14]. As sorption is the first step in the PV mechanism, determining the degree of swelling is essential to predict the transport mechanism and to investigate the effect of feed mixture composition on membrane performance [3]. Hydrophilic membranes used for the dehydration of alcohols may swell excessively in the presence of water, resulting in a loss of water-organic selectivity. Swelling can also cause plasticisation, making the membrane too flexible and further impairing its separation performance [14]. This effect can be mitigated by various techniques such as coating, grafting, crosslinking, plasma processing, chemical treatment, incorporation of inorganic fillers (zeolites, silica, carbon nanotubes, metal-organic frameworks), and the development of mixed matrix or hybrid membranes that exhibit reduced swelling while maintaining high flux [4,14]. Incorporating additives into polymeric PV membranes is an effective method for enhancing their surface and structural properties. Surfactant additives, known as surface-active agents, are commonly described using the tail-head model, where the tail represents the hydrophobic group, and the head represents the hydrophilic group [4]. On the other hand, inorganic membranes have better properties in terms of chemical, thermal, and mechanical resistance, making them suitable for use in more demanding conditions, e.g., in processes involving high temperatures, high pressure, and corrosive substances. Unlike organic membranes, swelling is not a problem with inorganic materials, and they have a much higher selectivity and flux rate compared to most polymeric materials. A good example is zeolite membranes, which have exceptional thermal and mechanical stability. Their homogeneous structure and uniform pore distribution enable efficient molecular sieving, which contributes to relatively intense mass transfer with high selectivity [15]. Despite their many advantages, the high cost, difficult reproducibility, and challenges in scaling up the production process limit their wider application.

To achieve a balance between cost and efficiency, mixed matrix membranes (MMMs) are now being produced. MMMs are composite membranes in which inorganic or highly selective porous particles are dispersed within a continuous polymer matrix to enhance separation performance. MMMs typically combine a hydrophilic polymer with fillers such as zeolites, silica, metal–organic frameworks (MOFs), or graphene oxide. These MMMs offer the advantages of both polymeric and inorganic materials and are considered among the most promising ethanol recovery solutions because of their strong hydrophobic nature [16–18]. The resulting membranes obtain new combined properties in which they retain the advantages of using polymer membranes, such as ease of manufacture, acceptable selectivity, and low production costs, while benefiting from the advantages of zeolite membranes, such as high permeability and selectivity. Composite membranes with a mixed matrix have combined separation mechanisms, including the solution-diffusion mechanism of polymeric membranes and the molecular sieving of zeolites [19].

Since zeolite 4A (also known as Na-LTA; Na-A) is the most commonly used zeolite in the adsorption process for the dehydration of bioethanol [19], the idea arose to develop membranes made of the same material and use them for dehydration with membranes. Hasegawa *et al.* [20] highlight in their work that Na-A type zeolite membranes showed exceptional results in the dehydration of bioethanol in the vapour permeation process at temperatures from 100 to 145 °C, achieving a relatively high flux of up to 37 $kg \cdot m^{-2} \cdot h^{-1}$ with a separation factor (β) of more than 10,000. Meanwhile, Charik *et al.* [21] achieved a flux of 8.49 $kg \cdot m^{-2} \cdot h^{-1}$ with a separation factor of 10900 using Na-A type zeolite membranes in the PV process at a temperature of 75 °C. One disadvantage of Na-A type zeolite membranes, mentioned by researchers Vane *et al.* [11], is their poor resistance to acids. Due to the low Si/Al ratio and the high aluminium content in the crystalline structure of this zeolite, this material has poor resistance to acids, which can have a negative impact on the longevity and stability of these membranes.

Zeolites from the chabazite group are another popular inorganic material that is often used to produce zeolite membranes. The zeolites CHA ZX0 and CHA ZX2 are used by Mitsubishi Chemical Corporation for the production of membranes sold under the trade name ZEBREX™ [11]. Hasegawa *et al.* [20] investigated various zeolite

crystallisation methods, different carriers, and production conditions and achieved a flux of up to 14.0 $kg \cdot m^{-2} \cdot h^{-1}$ with a separation factor of over 10,000 at a PV temperature of 75 °C. In addition to permeate flux and selectivity, a very important parameter for the quality of the membrane material is the ability of these parameters to remain at an acceptable level over a long period of time. Vane *et al.* [11] monitored the performance of membranes by recording changes in permeance and separation factor and testing Na-A and CHA membranes during PV and vapour permeation. The stability of the Na-A membrane during PV was tested over a continuous period of 39 days, with a 50% drop in permeability observed during the process. In this study, the researchers were unable to further test the durability of the CHA membrane due to technical problems. However, other researchers recorded a 24% decrease in permeance and even a 68% increase in selectivity over three days, suggesting that CHA membranes may be more stable and maintain their performance in an acceptable range over a longer period of time [22]. To obtain more reliable results on the long-term durability of CHA membranes, further testing over a longer period of time is required.

In their study, Vane *et al.* [11] came to the conclusion that higher temperatures during PV and vapour permeation lead to lower water permeability. However, in the case of vapour permeation in particular, the ability to increase both the temperature and the pressure of the feed solution can result in a significantly better permeate flux despite the decrease in permeation. A higher permeate flux means that a smaller membrane area is required to achieve the desired capacity, which can have a positive effect on the potential investment costs of production.

PVA is an organic polymer material with high abrasion and elongation resistance that is very easy to produce. The cross-linking of the polymer chains can be easily modified by physical or chemical processes to increase the selectivity and stability of the material. PVA is a hydrophilic polymer, and its hydroxyl groups enable the formation of hydrogen bonds, which gives this material a very high affinity for water. Ethanol molecules have a much lower diffusivity through PVA, which is why ethanol passes through the membrane much more slowly than water [15]. Hong *et al.* [23] investigated different ways of combining PVA and PES materials into composite membranes and observed changes in hydrophilicity depending on the mass fraction of PVA in the material, as well as changes in selectivity and permeate flux depending on the temperature during PV. They also analysed the stability of these parameters over a period of 28 days. The results showed that the hydrophilicity of the PVA-PES composite membrane decreased with increasing PVA content. At an absolute pressure of 300 Pa on the permeate side, PV was initially carried out at 50 °C, and then the temperature was increased to 80 °C, where a change in permeate flux from an initial 0.6 $kg \cdot m^{-2} \cdot h^{-1}$ to 1.6 $kg \cdot m^{-2} \cdot h^{-1}$ and a change in separation factor from 30 to 65 were observed. The increase in permeate flux and separation factor due to the increase in temperature was attributed to the increased diffusivity and mobility of the ethanol and water molecules, with the increase in temperature having a greater effect on water transport than on ethanol, as water has a lower activation energy compared to ethanol. The stability of the PVA-PES composite membrane was monitored over a period of 28 days, during which the membrane was immersed in a 90% ethanol-water solution and the permeate flux and separation factor were recorded regularly. Throughout the period, both parameters showed very little variation, with only a slight increase in permeate flux and a slight decrease in separation factor, indicating relatively good stability of the membrane during long-term use [23].

Although PVA is the most attractive and cost-effective polymer used in the dehydration of bioethanol, amorphous regions in the polymer tend to swell due to its anisotropic structure, which can have a negative impact on the separation factor over time. On the other hand, the production of pure zeolite membranes is very difficult and quite expensive. Therefore, the idea of combining popular materials such as PVA polymer and zeolite 4A emerged, resulting in a PVA/zeolite 4A composite membrane, which has much lower production costs and a simpler manufacturing process [24]. In the aforementioned study, the researchers investigated the effect of zeolite content on permeate flux and the effect of different temperatures on flux and separation factor. The membrane was tested by performing PV with a vacuum pump that maintained an absolute pressure of 400 Pa on the permeate side. When investigating the effect of zeolite content in the composite membrane with concentrations of 0–30% w/w at 80 °C, with 80% w/w ethanol in the feed solution, an increase in both separation factor and permeate flux was observed up to a zeolite content of 20% w/w [24]. As the zeolite content increased further, the permeate flux showed a positive trend, while the separation factor decreased significantly. Huang *et al.* explained this phenomenon by the fact that increasing the zeolite Na-A content increases the hydrophilicity of the membrane material by strengthening the interactions with the water molecules, which leads to greater mobility of the water molecules [24]. However, the simultaneous molecular sieving effect hinders the passage of ethanol molecules, as zeolite 4A has pore openings of 4 Å (0.4 nm), while the kinetic diameter of water molecules is 2.64 Å (0.264 nm) and the kinetic diameter of ethanol molecules is 4.30 Å (0.430 nm). Increasing the zeolite content above 30% (w/w) leads to agglomeration of the zeolite particles, which has a negative effect on the ability to separate ethanol and water molecules more effectively, resulting in a lower separation factor and increased permeate flux [24]. The effect of temperature on the process parameters was investigated at feed solution temperatures of 60, 80, and 100 °C during the dehydration of bioethanol in the PV process using the same PVA/zeolite 4A composite membrane. The results showed that increasing the temperature increased the permeate flux but decreased the separation factor. Increasing the temperature affected the mobility of both water and ethanol molecules [24]. Table 2 shows hydrophilic membranes made from various materials, with their process parameters tested in the dehydration of bioethanol.

Innovations in membrane fabrication have improved selectivity and permeability, enhancing the performance of PV systems. The development of high-performance membranes for ethanol dehydration is crucial for energy-efficient biofuel production. Jakubski *et al.* [9] investigate novel sodium alginate-based composite membranes incorporating magnetic selenide chromite fillers ($CuCr_2Se_4$, $ZnCr_2Se_4$, $CdCr_2Se_4$) and evaluate their PV performance. Incorporating magnetic fillers into polymer membranes can substantially improve the PV separation index (PSI) and separation factor (β) for ethanol-water mixtures. Previous studies on magnetic fillers in membranes have primarily focused on iron-based nanoparticles such as Fe_3O_4; however, these materials often suffer from poor dispersion, aggregation, and limited long-term stability, ultimately compromising membrane performance over time [9,25,26]. In their study, Jakubski *et al.* [9] report that incorporating selenide chromite fillers has a positive influence on the separation process. Morphological and physicochemical analyses confirm uniform filler dispersion at an optimal loading of 3 wt%, enhancing membrane performance. Membranes filled with $CuCr_2Se_4$ exhibit the highest PSI (1308 $kg \cdot m^{-2} \cdot h^{-1}$) and separation factor (490), which are significantly greater than those for membranes with $ZnCr_2Se_4$ (PSI = 244 $kg \cdot m^{-2} \cdot h^{-1}$, β = 78) and $CdCr_2Se_4$ (PSI = 425 $kg \cdot m^{-2} \cdot h^{-1}$). This enhanced performance can be attributed to the ferromagnetic nature of $CuCr_2Se_4$, which facilitates the alignment of water molecules and promotes the formation of preferential magnetic channels, thereby improving separation efficiency. Membranes filled with $CdCr_2Se_4$ consistently exhibit the highest flux (3.5 $kg \cdot m^{-2} \cdot h^{-1}$), followed by $ZnCr_2Se_4$ (3.0 $kg \cdot m^{-2} \cdot h^{-1}$), whereas membranes filled with $CuCr_2Se_4$ show the lowest flux values (2.8 $kg \cdot m^{-2} \cdot h^{-1}$). The introduction of selenide chromite fillers significantly enhances PSI, with membranes filled with $CuCr_2Se_4$ achieving the highest PV efficiency due to their ferromagnetic properties, which promote the formation of structured magnetic channels and better alignment and attraction of water molecules. In contrast, membranes filled with $CdCr_2Se_4$ show the highest flux, indicating weaker magnetic interactions that result in lower selectivity but higher permeability [9].

Ghorab *et al.* [4] focus on developing a novel polysulfone (PSF) dense hybrid membrane modified with the nonionic surfactants Tween 20 (T20) and Triton X-100 (X100) to improve PV dehydration of bioethanol. Tween 20 ($C_{58}H_{114}O_{26}$) is a nonionic polysorbate surfactant used in various industrial and scientific processes. It has one of the highest hydrophilic-lipophilic balance values, indicating its exceptional hydrophilic properties. Triton X-100 ($C_6H_{26}O_2$) is a nonionic surfactant synthesised by polymerising octylphenol with 100 units of ethylene oxide.

Table 2. Hydrophilic membranes for the dehydration of bioethanol by pervaporation.

Water in feed (wt%)	Active layer	Membrane support	Temperature (°C)	Flux (kg m^{-2} h^{-1})	Separation factor ($\beta_{water/ethanol}$)	Reference
10	Zeolite X	Zeolite X	65	3.37	296	[12]
10	Ultrathin zeolite X	/	65	3.37	415	[12]
10	ECN silica	/	70	2.33	71	[59]
10	Chabazite	Asymmetric α-Al_2O_3	75	14.0	> 10 000	[20]
10	NaY zeolite	NaY zeolite	75	2.10	105	[60]
10	Chabazite	Symmetric multiple	75	2.2	3900	[24]
10	Heterogenous PA	PAN	70	13.90	4491	[61]
10	CS	GG/PAN	80	0.80	2329	[62]
10	PVA	PES	80	1.60	65	[23]
15	PVDF hollow fiber	PVDF hollow fiber	50	1.29	40	[63]
15	PVAeCA blend	PVAeCA blend	45	0.21	40	[63]
5	Hybsi®	/	70	1.70	139	[64]
10	Silica-CS hybrid	Silica-CS hybrid	30	0.59	-	[65]
20	PVA/zeolite 4A	/	80	1.50	838	[24]
10	CS-$TiCl_4$-DHHPPA	PAN	77	1.40	730.0	[66]
10	CNTs	PA (blend)	22	1.20	22.0	[67]

It is recognised for its effectiveness in the bioremediation of sites contaminated with hydrophobic hydrocarbons. The PV results showed that incorporating 0.5 wt% T20 into PSF significantly improved the total flux and PSI of PSF/T20 to 0.226 $kg \cdot m^{-2} \cdot h^{-1}$ and 46.58 $kg \cdot m^{-2} \cdot h^{-1}$, respectively. Similarly, the total flux and PSI of hybrid membranes containing X100 increased to 0.110 $kg \cdot m^{-2} \cdot h^{-1}$ and 43.68 $kg \cdot m^{-2} \cdot h^{-1}$. Consequently, the developed PSF/T20 membranes demonstrated greater potential for bioethanol dehydration compared to PSF/X100 membranes [4].

Yap Ang *et al.* [27] developed a series of advanced polyurea composite membranes using interfacial polymerisation of various amine monomers (ethylenediamine (EDA), diethylenetriamine (DETA), and 2,2′,2″-nitrilotriethylamine (NTEA)) with diisocyanate monomers (1,6-diisocyanatohexane (HDI), m-xylylene diisocyanate (XDI), and 1,3-bis (isocyanatomethyl)cyclohexane (BIMC)) on modified polyacrylonitrile (mPAN) supports. These membranes were optimised and evaluated for PV -based dehydration of a 90 wt% aqueous ethanol solution. Polyurea membranes offer an exceptional combination of mechanical strength, thermal stability, and chemical resistance. Amine monomers impart excellent performance characteristics to the membranes, including high water selectivity, robust permeation rates, and long-term operational stability. The distinct chemical structures of the diisocyanates influence the degree of cross-linking, rigidity, and hydrophilicity of the resulting polyurea network, ultimately impacting membrane performance. The results of this study showed that the thin film composite (TFC) DETA-XDI membrane exhibited the best balance between permeation flux and water selectivity, achieving a permeation rate of 0.462 $kg \cdot m^{-2} \cdot h^{-1}$ at 30 °C with a water concentration in the permeate of 99.1 wt%. At 70 °C, the flux increased to 0.783 $kg \cdot m^{-2} \cdot h^{-1}$ with 99.3 wt% water selectivity [27].

MOFs have received extensive attention in the membrane field due to their high porosity, tunable structures, and pore sizes. However, their weak hydrothermal and chemical stability limit their application in the separation of liquid mixtures [28]. These limitations motivated the research by Zhang *et al.* [28], who included zeolitic imidazolate frameworks (ZIFs) with zeolite topology in their study. ZIFs are among the few water-stable MOF materials due to the presence of metal–azole frameworks [28,29]. Among all ZIF materials, ZIF-8 is most suitable for the separation of ethanol-water mixtures because its pore diameter (0.34 nm) lies between the molecular dynamic diameters of ethanol (0.43 nm) and water (0.30 nm). ZIF-8 also offers several other advantages, including simple preparation methods, adjustable morphologies, and good compatibility with organic polymers. Zhang *et al.* [28] designed a stable modified ZIF-8 (MZIF-8) as an interlayer in composite membranes, using poly(4-styrenesulfonic acid) (PSS) to link ZIF-8 nanoparticles. They used ceramic hollow fibre as the support for the composite membrane due to its excellent mechanical and thermal stability. The membrane flux and separation factor increased with rising operating temperature (40–70 °C). As the ethanol feed concentration decreased, the total flux increased from 0.81 to 4.47 $kg \cdot m^{-2} \cdot h^{-1}$, while the separation factor decreased from 318 to 127. The selectivity of the polyamide/MZIF-8 (PA/MZIF-8) membranes for water-ethanol mixtures was found to be about five times higher than the ideal water-ethanol selectivity, demonstrating that ethanol permeance in the membrane matrix was hindered by the preferential water adsorption of the PA/MZIF-8 membranes. These composite membranes not only exhibited excellent dehydrating performance for ethanol-water mixtures, but also operational stability under high temperature and acidic conditions. Therefore, these membranes have great potential for industrial applications [28].

Pervaporation using polymer–inorganic hybrid membranes offers a promising low-energy alternative, provided that the membrane exhibits both high flux and selectivity for alcohols. Naveed *et al.* [18] demonstrate that incorporating a porous liquid (PL) form of zeolitic imidazolate frameworks (ZIF-67) into polydimethylsiloxane (PDMS) MMMs enables simultaneously high flux and selectivity for ethanol dehydration via PV. PLs have emerged as an innovative class of materials that combine the fluidic behaviour of liquids with the intrinsic porosity typically associated with solids. PLs offer several advantages, such as chemical and thermal stability, good dispersion behaviour, tunable selectivity, and operational versatility across a wide range of separation processes. Pervaporation tests using a 6 wt% ethanol/water feed showed that the 40 wt% ZIF-67-PL membrane achieved a total flux of 3.5 $kg \cdot m^{-2} \cdot h^{-1}$ and a separation factor of 19.8 at 65 °C, corresponding to approximately a 170% increase in flux and a 205% enhancement in separation factor compared to pristine PDMS. Benchmarking against state-of-the-art PDMS-based MMMs highlights ZIF-67-PL/PDMS membranes as a high-performance, scalable platform for bioethanol dehydration and, more broadly, for next-generation porous-liquid-enabled separations [18].

Inspired by the specific properties of ionic liquids (ILs) and the self-assembled ionic liquids (SAILs) nanostructure, Ali *et al.* [30] constructed PV membranes with a self-assembled ILs-PVA micelle nanostructure, achieving high ethanol dehydration performance. The formation of the ILs-PVA micelle significantly influenced membrane surface morphology, roughness, and water contact angle, providing an additional transport channel for the membrane. The ILs can form strong hydrogen bonds with water and disrupt the hydrogen bonding in the EtOH-H_2O azeotropic mixture, which is beneficial for improving selectivity. Under optimal conditions, at the critical micelle concentration (cmc) point, the PVA-ILs membrane exhibited a superior separation factor of 1627, along with a flux of 0.684 $kg\ m^{-2} \cdot h^{-1}$ at 50 °C [30].

Kakooei *et al.* [31], in their study, introduced a novel PV membrane for bioethanol dehydration, incorporating MXene-reinforced PVA nanofibres. MXene is a two-dimensional nanomaterial. These transition metals exhibit unique hydrophilic and conductive properties. PVA nanofibres can effectively absorb water from ethanol due to their high surface area and water absorption properties.

PVA MMMs with MXene nanosheets show a significant increase in water flux and separation factor for ethanol dehydration, suggesting that the incorporation of 2D nanomaterials into PVA can enhance its PV performance. These composite membranes can achieve a permeate flux of 0.862 kg $m^{-2} \cdot h^{-1}$ and a separation factor of 467.2 for 90 wt% ethanol dehydration at 30 °C, representing improvements of 46.1% and 60.3%, respectively, over pristine PVA membranes [31].

Ceramic membranes represent a smaller but technically significant niche in bioethanol dehydration, particularly for PV and vapour permeation under harsh conditions. Compared to polymeric membranes, ceramic systems are preferred when high thermal or chemical stability, long lifetime, or operation with aggressive streams is required. The main industrial and technology players that have worked with ceramic membranes for ethanol dehydration are Sulzer Chemtech (Switzerland), Pervatech/NX Filtration (Netherlands), Mitsubishi Chemical/Mitsubishi Heavy Industries (Japan), TAMI Industries (France), and Fraunhofer IKTS (Germany) [32,33].

Mechanism of mass transfer through various membranes

Diffusion through non-porous polymers is quite similar to mass diffusion through a liquid solvent, especially when the dissolved phase is gaseous. Many types of gases and liquids are soluble in polymeric materials. The diffusing substance dissolves on one side of the polymer membrane, permeates the membrane, and is desorbed on the other side of the membrane. The macromolecules of polymers are in a state of constant motion. Therefore, the intensity of transfer of the solute through polymers depends mainly on the intensity of movement of the polymer chain, i.e., the free intermolecular space through which the solute moves, as well as the driving force, i.e., the difference in equilibrium concentrations on both sides of the polymer membrane. If the substance dissolved in the membrane is a gas, the equilibrium concentration in the polymer is proportional to the partial pressure of the component in the gas. This behaviour is of great importance when a vacuum is applied on the permeate side during bioethanol dehydration, as a change in pressure in the system can intensify the mass transfer process and thus increase the permeate flux [34].

Zeolites are aluminosilicates with highly porous crystalline structures consisting of a three-dimensional network of tetrahedrally orientated units. They have very well-defined spatial properties, so that cavities with precisely defined dimensions and shapes are present in this network, into which some molecules can penetrate while others remain outside, which is why they are also known as molecular sieves. Conceptually, the structure of zeolites can be imagined as a pure network of silicon and oxygen in a tetrahedral arrangement, with a silicon atom replaced by an aluminium atom at certain points [19,35].

The mechanism of mass transfer through zeolitic membranes includes molecular sieving, diffusion, and adsorption-controlled permeation. When separating with small-pore zeolites, the most common mechanism is molecular sieving, where molecules larger than the pore size are retained while smaller molecules are allowed to pass through. The diffusion and adsorption permeation mechanisms are such that zeolites have larger pores relative to the molecules to be separated, so that separation is based on the interaction between the molecules passing through the zeolite and the zeolite itself. Zeolite membranes can be used for separation processes in both liquid and gaseous systems [19].

Pervaporation in the dehydration of bioethanol

PV is a membrane separation process in which mass transfer takes place through a dense, non-porous membrane. The mass transfer is based on the intensity of the physico-chemical interactions between the components of the feed solution and the membrane. Therefore, the selection of the membrane material that best fulfils the purpose in each individual case is crucial for optimum process performance. The word "pervaporation" is a combination of two words: permeation and vaporisation, and clearly indicates the mechanism of mass transfer through the membrane. In PV, the feed solution is in liquid form, while the permeate is in the vapour phase. Although the mechanism of mass transfer in PV is not fully understood, the solution–diffusion model is widely accepted. Since the feed solution is liquid and the permeate is gaseous, it is assumed that vaporisation takes place somewhere in the membrane mass. After vaporisation, further transfer occurs by molecular diffusion, followed by desorption on the permeate side. Applying a vacuum on the permeate side lowers the partial pressure on the permeate side, which intensifies the vaporisation process [10].

The process parameters that are most frequently controlled during PV are the flow rate and temperature of the feed solution, and the maintenance of an adequate vacuum on the permeate side. Figure 2 shows the generalised process parameters to provide a simpler understanding of the PV process in the dehydration of bioethanol.

The temperature of the feed solution is often kept in the range of 60–90 °C [10,15,21] to ensure an adequate driving force for mass transfer, namely the difference in partial pressures of the water vapour. Due to the endothermic nature of the PV process, the retentate has a lower temperature than the feed solution. Therefore, if the retentate needs to be recirculated to remove additional water, an additional heater is often required to maintain the optimum temperature of the feed solution for the PV process.

As the feed solution is in a liquid state, increasing the pressure of incompressible liquids does not affect the concentration of the substances present and therefore has little effect on increasing the permeate flux. By installing a pump, however, the flow velocity of the liquid can be influenced, and the flow regime can be changed. It has been shown that a turbulent flow regime of the feed solution contributes significantly to increasing the permeate flux. In subsequent studies [10,36], it was found that the most suitable flow rate is between 3 and 9 L/min to achieve an optimal permeate flux with acceptable values of the

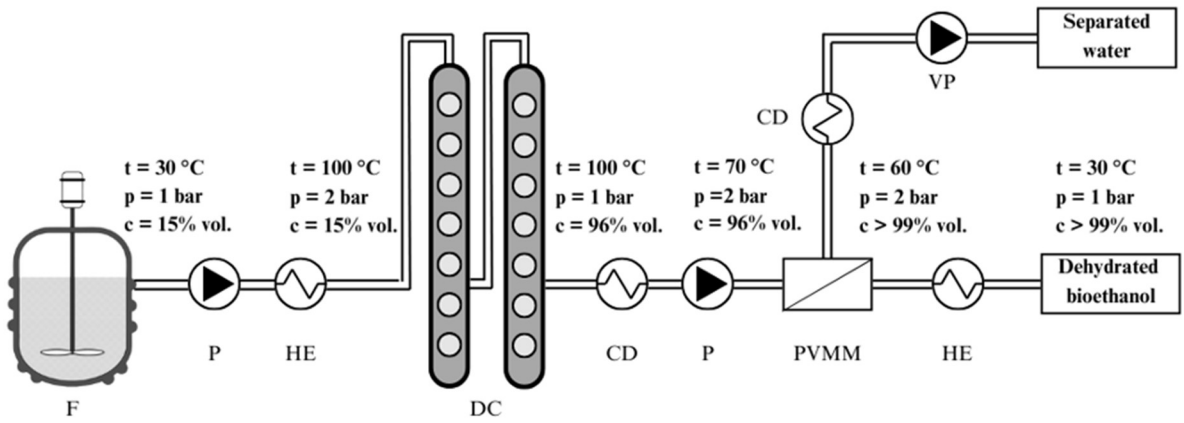

Figure 2. Schematic representation and general process parameters in the dehydration of bioethanol by pervaporation, where the following is shown: F - Fermenter; P - Pump; HE - Heat Exchanger; DC - Distillation Column; CD - Condenser; PVMM - Pervaporation Membrane Module; VP - Vacuum Pump.

separation factor. In industry, the partial vapour pressure on the permeate side is generally reduced with a vacuum pump. The absolute pressure on the permeate side should normally be in the range of 1–8 kPa. A lower pressure on the permeate side can increase the permeate flux, but care must be taken to achieve a balance between operating and capital costs and flux so that the price of the final product is not affected. Achieving a lower vacuum requires the purchase of a more powerful and more expensive vacuum pump, as well as higher energy consumption for its operation and for the subsequent condensation of the vapour at lower pressure due to the increased heat of the phase transformation. The vacuum pump is often switched off at regular intervals to reduce energy consumption [10].

Pervaporation with hydrophilic membranes (e.g., PVA-based, NaA zeolite, and mixed-matrix membranes) is widely used for dehydration of bioethanol streams prior to final fractionation, reducing water content and improving the separation of higher alcohol by-products such as fusel oils. Removing water shifts vapour-liquid equilibria and increases relative volatility differences among ethanol and C3–C5 alcohols, facilitating downstream recovery of fusel oil fractions. Recent studies also emphasise hybrid distillation- PV schemes to lower energy consumption and enable valorisation of higher alcohol co-products. This approach is particularly effective for fermentation-derived ethanol, where multicomponent azeotropes complicate conventional rectification [37–39].

Pervaporation performance in bioethanol dehydration is strongly influenced by operating parameters that affect both flux and selectivity. Increasing temperature generally enhances permeation flux due to higher diffusivity and vapour pressure, although it may reduce selectivity because of membrane swelling and decreased sorption selectivity. Feed concentration is critical, as higher water content in the feed increases the driving force and thus water flux, while high ethanol concentrations can reduce separation efficiency. The effect of feed concentration on PV membrane performance depends on the type of module used – either hydrophilic or hydrophobic – with the effect being more pronounced in hydrophobic membranes. The PSI shows a nonlinear trend with increasing feed concentration. Feed flow rate affects concentration polarisation; higher flow rates typically improve mass transfer at the membrane surface and maintain a higher effective driving force. Permeate pressure is an important factor, as it defines the driving force for both mass and energy transfer across the membrane. Lower permeate pressure (i.e., higher vacuum) increases the chemical potential gradient across the membrane, significantly enhancing flux and separation factor due to an increased driving force for component transport, as reported by many researchers [16,40,41]. High vacuum, or the minimum operating permeate pressure, is directly linked to energy cost. There is a trade-off between vacuum pump energy consumption and ethanol flux to achieve maximum efficiency. Membrane material plays a decisive role, with hydrophilic membranes (e.g., PVA, zeolite-based) favouring water transport, while structural properties such as free volume and crosslinking determine selectivity and stability. Ultimately, the driving force in PV is the partial vapour pressure difference of components across the membrane, which integrates the effects of temperature, composition, and pressure, and governs overall separation efficiency [16,37,42].

Vapour permeation in the dehydration of bioethanol

Recently, more practical importance has been attached to vapour permeation in the dehydration of bioethanol, as it does not require prior condensation and can be integrated directly into the distillation column. Furthermore, there is no endothermic effect when the vapour passes through the membrane, so there is no need for additional heating of the feedstock mixture due to a temperature drop, which is not the case with PV [43]. An important common property of membranes in both processes is that a higher permeate flux can be achieved by reducing the membrane thickness and increasing the surface area through which mass transfer occurs [10].

Vapour permeation is a membrane process in which the feed solution consists of a mixture of vapours or steam and gases. The process has many similarities with PV and gas permeation, and similar membranes can be used. The dehydration of bioethanol by vapour permeation uses hydrophilic membranes that mainly allow water vapour to pass through. The transfer mechanism is generally

accepted as a solution-diffusion model, similar to PV [10]. It is very important to carefully control the pressure of the feed solution, the pressure on the permeate side, and the temperature at which the process is carried out. Figure 3 shows the general process parameters, which are a simplified representation of the vapour permeation process for the dehydration of bioethanol [43,44].

The pressure of the feed solution (a vapour mixture) is an important parameter in vapour permeation because ethanol-water vapour is a compressible liquid, which means that an increase in pressure leads to a higher concentration of the components near the membrane. When the concentration of components is expressed by partial pressures, it is clear that a greater difference in partial pressures between the feed solution side and the permeate side contributes to a higher permeate flux [10]. In order to achieve a higher pressure of the feed solution, a compressor is usually used after the distillation column, which first increases the pressure with the help of electrical energy and, as a result of the compression, also raises the temperature of the feed solution. The literature suggests the use of a heat exchanger between the compressor and the membrane module to adjust the temperature of the feed solution to the optimum temperature for vapour permeation [43]. According to the literature, the absolute pressure of the feed solution is typically between 110–560 kPa [1,43–45], while the absolute pressure on the permeate side is usually not more than 10 kPa and is often much lower [1,10].

According to the literature [1,43–45], the temperature of the feed solution is usually in the range of 80–145 °C, with higher temperatures usually contributing to a higher permeate flux, which is often accompanied by a decrease in the separation factor. In contrast to PV, the temperature of the retentate is not reduced during vapour permeation for bioethanol drying compared to the feed solution. After it has passed through the membrane module, the retentate vapour must be condensed, and higher retentate temperatures can further increase energy consumption during condensation. This should be carefully considered when designing the system and integrating the energy requirements of the process.

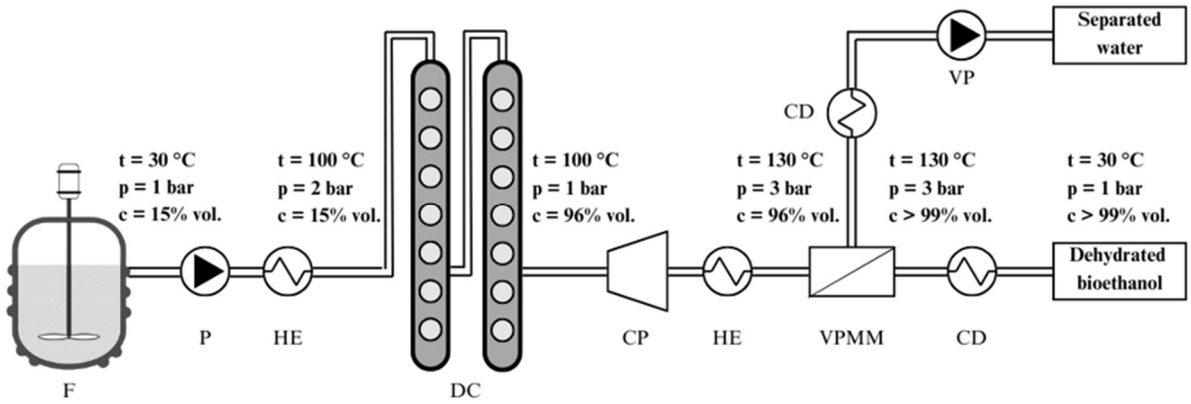

Figure 3. Schematic representation and general process parameters in the dehydration of bioethanol by vapour permeation, where the following terms stand for: F - Fermenter; P - Pump; HE - Heat Exchanger; DC - Distillation Column; CP - Compressor; VPMM - Vapour Permeation Membrane Module; CD - Condenser; VP - Vacuum Pump.

Hybrid technologies for the dehydration of bioethanol

Distillation followed by PV has proved to be the most economical hybrid scheme. A hybrid configuration can provide up to 41% energy cost savings compared to conventional extractive distillation in alcohol dehydration [16]. Hybrid processes investigated so far include PV–distillation hybrids, vapour permeation–distillation hybrids, microbubble distillation, membrane dephlegmation, adsorption/desorption, and ohmic-assisted hydrodistillation.

The PV –distillation hybrid involves separation through PV followed by distillation to further enrich the feed stream. Advantages of this hybrid process include flexibility with respect to load and feed conditions, suitability for use in multistage systems, and no risk of product contamination. However, this hybrid also has disadvantages, such as concentration polarisation on the feed side and temperature reduction along the module [16,42,46]. Leon *et al.* [39], in their study, investigated a distillation-PV hybrid in a single unit (DPSU) that incorporates a PV unit inside a distillation column. The DPSU system was applied to the separation of the ethanol-isopropanol-water mixture. The inverted separation order of isopropanol and water using the DPSU system was observed, which contrasted with traditional distillation. Moreover, the removal of water by the PV part of the system resulted in a reduction in the volatility of the lightest components of the mixture and shifted characteristic distillation points [39,47].

Kujawska *et al.* [47] investigate dehydration by PV using the ECO-001 pilot plant. The pilot-scale properties of a hydrophilic composite poly(vinyl alcohol) (PVA) membrane (PERVAPTM 2200) in contact with wet raw bioethanol are presented. The wet raw bioethanol consisted of ethanol (82.4–89.6 wt%), water (5.9–8.5 wt%), methanol (2.3–6.9 wt%), cyclohexane (0.2–2.4 wt%), higher alcohols (0.2-1.3 wt%), and acetaldehyde (0.004–0.030 wt%). All experiments were conducted using a SULZER ECO-001 plant equipped with a 1.5 m^2 membrane module. It was found that a low feed flow rate reduced dehydration efficiency, as the enthalpy of evaporation caused a significant temperature drop in the module (around 25 °C at a feed flow rate of 5 kg/h). The separation coefficient during PV ranged from 600 to 1200,

depending on the feed composition. Increasing the temperature enhanced the permeation flux and reduced the time required to reach the desired level of dehydration. It was shown that dehydration by PV using the ECO-001 pilot plant is an efficient process, which also enables investigation of the influence of various parameters on process efficiency [47].

In the vapour permeation–distillation hybrid process, separation is performed through vapour permeation followed by distillation to further enrich the feed stream. In this process, there is no phase change during permeation, and compared with the pervaporation–distillation hybrid, this process has a lower risk of concentration polarisation on the feed side. Disadvantages of this hybrid process include the possibility of forming a stagnant condensate film on the feed side and a strong dependence on feed pressure [16,46].

Microbubble distillation is a process in which hot air microbubbles are introduced, causing the water to vaporise and concentrate the feed. This process has lower energy requirements. It is suitable for heat-sensitive components, and separation can be achieved at temperatures lower than the boiling point of the liquid, allowing elimination of azeotropes. However, microbubbles have complex dynamics [16,48,49].

Membrane deflegmation is a combination of distillation and PV in a single unit. Vapour feed enters a vertically oriented membrane, and condensed vapours move downward, producing countercurrent contact. This is a thermodynamically efficient process and eliminates azeotropes, but it has low recovery and operational complexity [16,50,51].

Ethanol dehydration can also be effectively performed by an adsorption/desorption process using molecular sieves as adsorbents. The adsorption/desorption process involves the adsorption of a selected component onto the adsorbent material, followed by desorption to obtain a concentrated solution. Adsorption takes advantage of the enrichment of the adsorbent surface by sorbed substances at the interface between solid and liquid. Desorption is performed to regenerate the adsorbent without significant loss of its adsorptive properties. However, the desorption step requires high temperature and/or low pressure, which significantly affects overall process costs [16,47,52,53].

Ohmic-assisted hydrodistillation involves ohmic heating via electrodes to heat the solution for distillation. The advantages of this process include shorter extraction time, high thermal efficiency, reduced operating costs, and environmental friendliness. Disadvantages include the need to add electrolytes to less conductive feed, safety and scale-up concerns, and high capital investment [16,54,55].

Extractive distillation (ExD) is typically used for separating non-pressure-sensitive azeotropes. ExD enables the separation of complex mixtures by introducing an additional solvent (entrainer) at the top of the column. The added component alters the activity coefficients of the mixture components in the liquid phase, thereby modifying their relative volatilities [47]. Kiss and Szuszwalak [56] used dividing-wall columns (DWC) for ethanol dehydration via ExD and azeotropic distillation (AD). Process efficiency was assessed using Aspen Plus software and sequential quadratic programming methods. Ethylene glycol and *n*-pentane were used as mass-separating agents during the dehydration of a mixture containing 85 mol% ethanol. The proposed methods enabled the production of ethanol with 99.8 wt% purity [56]. In this study, simulation results showed energy savings of 10–20% compared with typical extractive and azeotropic distillation setups. The authors concluded that the proposed concept is more profitable when constructing a new ethanol dehydration plant, as investment costs for modernising an existing plant would exceed potential profits. They claimed that DWC can successfully intensify the efficiency of the distillation process due to lower investment and operational costs, as well as reduced equipment requirements [56].

Novita *et al.* [57] investigated the performance of an ExD column coupled with PV during the ethanol dehydration process. Glycerol was used as the entrainer in ExD. The PV operation, performed with a cellophane membrane, aimed to separate the glycerol-water mixture. This study showed that the hybrid ExD-PV configuration can achieve savings of up to 25% in total annual costs and 41% in energy expenditures compared with the standard configuration (ExD combined with a recovery column) [47,57].

CONCLUSION

Pervaporation and vapour permeation have proven to be effective membrane separation processes for dehydrating bioethanol and achieving high purity. Both processes operate on the solution–diffusion model, where the choice of hydrophilic membrane material is essential for selective water removal. Among the membranes evaluated, zeolite Na-A exhibited the highest performance, achieving a permeate flux of 37 kg $m^{-2}h^{-1}$ and a separation factor exceeding 10,000 in vapour permeation, and 8.49 kg $m^{-2}h^{-1}$ with a separation factor of 10,900 in PV. Chabazite-zeolite and polymeric heterogeneous polyamide membranes also demonstrated high flux and selectivity. Operating conditions significantly influence membrane performance: increasing temperature and feed flow rate generally enhance flux but reduce the separation factor, while decreasing permeate-side pressure increases flux in both processes. In vapour permeation, feed pressure positively affects flux due to the compressibility of vapour, unlike in PV, where liquid incompressibility limits this effect.

Quantitative analyses indicate that membrane-based dehydration processes, particularly PV and vapour permeation, can reduce energy consumption by approximately 30–50% compared to conventional distillation and molecular sieve adsorption. These improvements result in lower operating costs and competitive overall economics, suggesting that membrane systems can serve as viable alternatives or partial replacements in bioethanol dehydration, especially in hybrid process configurations [11,32,33].

Only hydrophilic membranes are used in these processes, made from organic, inorganic, or hybrid materials. While organic membranes are cost-effective, they have lower stability and performance. Inorganic

membranes, although costly, offer superior durability and separation efficiency. Hybrid membranes combine the advantages of both, showing potential for improved process efficiency and cost reduction in industrial applications.

Hybrid systems that combine membrane separation with distillation are considered promising because of their enhanced energy efficiency and cost-effectiveness in bioethanol purification. These configurations can reduce energy consumption by up to 41% compared to conventional ExD used for alcohol dehydration.

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PREGLEDNI RAD

PRIMENA MEMBRANSKIH PROCESA U DEHIDRATACIJI BIOETANOLA

Bioetanol predstavlja izuzetno važnu sirovinu na svetskom tržištu koja se koristi u različitim industrijama. Procesi prečišćavanja koji se najčešće primenjuju u savremenim biorafinerijama uključuju destilaciju za izdvajanje etanola, a zatim adsorpciju na zeolitima za dehidrataciju bioetanola. Oba procesa su veoma energetski zahtevna. Membranski separacioni procesi imaju značajan potencijal da zamene obe faze u proizvodnji bioetanola, čime bi se mogli značajno smanjiti operativni troškovi i ukupni troškovi proizvodnje. U ovom radu opisana je primena pervaporacije i parne permeacije u procesu dehidratacije bioetanola. Cilj je povećanje koncentracije etanola sa 96 vol.% na izlazu iz destilacione kolone na više od 99 vol.% primenom hidrofilnih membrana koje selektivno propuštaju molekule vode i na taj način ih uklanjaju iz bioetanola. Na osnovu postojeće literature određeni su optimalni procesni parametri, kao što su temperatura, pritisak, protok i pritisak na permeatnoj strani. Pored toga, prikazane su performanse različitih organskih, neorganskih i kompozitnih membrana, kao i razmatranje održavanja ovih parametara i opadanja performansi materijala tokom dužeg perioda upotrebe.

Ključne reči: pervaporacija, parna permeacija, zeolitne membrane, kompozitne membrane, polimerni materijali.