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Review Article

Exploring Membrane Pervaporation Separation: A Review on Obtaining Combustible Ethanol and Butanol from Fermentation Broths

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ABSTRACT

Pervaporation is an advanced membrane-based separation technique to purify complex mixtures (e.g., those with azeotropes or thermolabile compounds) which would otherwise require involved sequences of conventional separation operations such as distillation or extraction. Pervaporation is particularly well suited for some alcohol + water mixtures since it is not limited by the presence of the azeotrope, while improving energy efficiency and reducing operating costs. Furthermore, its coupling with biomass fermentation for biofuels production alleviates product inhibition, thereby increasing yield by up to 67%. This review focuses on the performance of pervaporation membranes, primarily those based on polydimethylsiloxane (PDMS), for the separation of alcohols from fermentation broths, reporting flux values of up to 203.76 g/m² h and a separation factor of up to 147. Additionally, the effects of composition and temperature are evaluated. Factors influencing process efficiency are also analyzed, and emerging technologies, new bacterial strains, and biomass sources are highlighted as strategies to enhance alcohol fuel production. Finally, examples are presented where pervaporation has significantly contributed to improving biofuel production.

Keywords: Fermentation broth, fuel alcohols, membrane material, PDMS, pervaporation

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INTRODUCTION

Pervaporation is a separation technique for the selective removal of some components from liquid mixtures by means of membranes. This technique is well-suited

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for mixtures where conventional separation techniques (such as distillation, extraction, adsorption, and absorption) are difficult to implement due to physicochemical constraints, high energy consumption, or environmental impact. Pervaporation membranes offer a promising approach for biofuel separation and purification. This technology displays several advantages, including efficient separation with lower energy consumption, minimal environmental impact, and prevention of microbial contamination, as it does not require excessive heating, toxic solvents, or additional chemicals. Furthermore, it allows for the continuous extraction of bioalcohols directly from fermentation broths (Lee & Lin, 2024).

In comparison, traditional methods, such as gas stripping and distillation (Figure 1), present challenges such as low selectivity, the need for large gas flow rates, and significant energy demands for the condensation stage. On the other hand, liquid-liquid extraction (Figure 1) presents problems such as solvent loss due to volatility, toxicity to microorganisms, and the formation of stable emulsions that are difficult to break. Similarly, adsorption is limited by low selectivity and the rapid saturation of the adsorbent material caused by the co-adsorption of other compounds. Therefore, pervaporation membranes (Figure 1) are proposed as a very attractive alternative to overcome the previously described limitations and, thus, lay the foundation for the development of a sustainable and long-lasting process (Lee & Lin, 2024).

Pervaporation is especially useful for the purification of azeotropic or thermolabile mixtures, mixtures of species with close molecular shape/chemical functionality, and components in trace concentrations (He et al., 2020; Imad & Castro-Muñoz, 2023). In

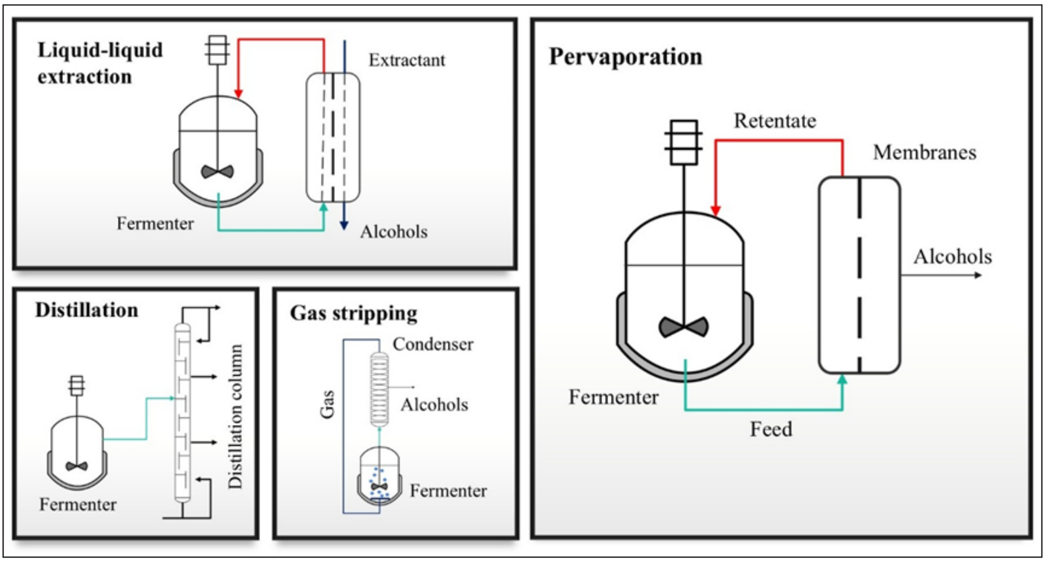

Figure 1. Schematic representation of pervaporation, gas stripping, liquid-liquid extraction processes, and distillation

this process, the components in a liquid mixture with a stronger affinity for the membrane material first solubilize and then diffuse through the membrane to exit as vapor on the other side because of a reduced pressure; the vapor stream is then condensed, and the compounds are recovered as liquids. Contrarily, components that interact weakly with the membrane remain in the liquid stream, which facilitates coupling of pervaporation with continuous processes. Pervaporation involves not only mass transfer but also heat transfer, provided by the feed liquid stream through its enthalpy of vaporization (Anilkumar & Roy, 2024; Castro-Muñoz, 2024; Silva et al., 2021).

Pervaporation separation may be coupled with other physical and/or chemical processes to increase productivity (Kusmiyati & Susanto, 2015). For example, pervaporation can be integrated with bioreactors to provide high-quality biofuels. In the conventional process of bioethanol production, a filtered fermentation broth is subjected to distillation yielding a circa (ca.) 96 mol % ethanol solution that cannot be further purified by distillation due to the presence of an azeotrope and, consequently, cannot be used as biofuel because of the potential corrosion in the engine and/or storage tank (Yang et al., 2024); furthermore, the high energy cost of distillation impairs the economy of the process with respect to fossil fuel production (Kaewkannetra et al., 2012; Kalahal et al., 2021). Besides overcoming these disadvantages and making a more energy-efficient and competitive process, pervaporation can be implemented as a simultaneous fermentation-separation system, allowing for the removal of alcohol *in situ* and making inhibition of microorganisms during the fermentation process less likely (Jaimes et al., 2021; Van Goethem et al., 2023). Therefore, an increase in yield, productivity and economic efficiency of the overall process is expected (Shin et al., 2015; Van Goethem et al., 2023).

Alcohol concentration in the fermentation broth has been identified as a key parameter in the coupled fermentation-pervaporation process (D. Liu et al., 2015; Fu et al., 2016; Jaimes et al., 2021; Jung et al., 2018; Setlhaku et al., 2013; Wagner & Gasch, 2023; Yang et al., 2024). In particular, the concentration of the recovered alcohol (i.e., in the permeate stream) is directly proportional to the concentration of the alcohol in the broth (i.e., the feed stream). However, there is a trade-off between alcohol flux and selectivity (Z. Zhang et al., 2021) because of a possible increased diffusion of the smaller water molecules (Dong et al., 2014; L. Liu et al., 2021; Wagner & Gasch, 2023). Total flux, separation factor, and selectivity are also directly proportional to the temperature of the pervaporation cell. The increased flux is related to a higher solubility and diffusion rate of the permeable compound on the surface and bulk of the membrane, respectively (Kaewkannetra et al., 2012), due to an increased molecular mobility of the polymer chains at higher temperatures (Z. Zhang et al., 2021), which, in turn, leads to enlarging the free volume of the membrane (Dadi et al., 2018; Yang et al., 2024). For example, using PDMS membranes, Trinh et al. (2019) reported an increase in flux from 50.1 to 90.8 g/m^2 h, and in separation factor from 1.9 to 2.3 as the temperature was raised from 20 to 40°C. Similarly, Lazarova et al. (2012) reported an increment in separation factor with temperature (from 25 to 75 °C) with poly(octylmethylsiloxane) (POMS) membranes. However, as the temperature approached 95°C, the separation factor showed values similar to those obtained at 50°C. On the other hand, using carbon nanotube (CNT)-loaded PDMS membranes (Xue, Wang, et al., 2016) questioned the simple relationship between alcohol flux/separation factor with temperature, arguing that weak water-ethanol hydrogen bonding interactions would not lead to the coupling between these two molecules, a phenomenon observed mainly in porous membranes. Ethanol molecules, being more voluminous, reduce the number of water molecules passing through the membrane because the interaction between ethanol and water would be weaker. Therefore, the permeability of the membrane is altered, favoring the passage of ethanol compared to water. Therefore, the differences in molecular size and hydrogen bonding interactions are key factors that explain why ethanol molecules can reduce the passage of water through the membrane (Xue, Wang, et al., 2016).

Alcohol concentration and temperature, however, are not the only factors that can be exploited to impact the flux and separation factor (or selectivity) of the membrane. The objective of this review is to highlight other variables that can be tuned to obtain high-quality fuel alcohols (bioethanol or biobutanol) through the coupled fermentation-pervaporation processes, such as the addition of some fermentation by-products or the modification of the alcohol-membrane interactions, which are paramount in the pervaporation process. Furthermore, the use of other strategies to improve fuel alcohol yield and productivity is highlighted, such as new bacterial strains, lignocellulose-based biomass to ensure food security, or the coupling of other separation processes to the fermentation-pervaporation system. Finally, several cases are presented where the coupled system produces not only the biofuel but also value-added products, making pervaporation a more attractive technique.

A comprehensive review of the scientific literature published between 2012 and 2024 was conducted. The search included keywords such as "biofuel", "bioethanol", or "biobutanol", and "fermentation" and "pervaporation". Additionally, to broaden the scope of the results, the keyword "fermentation by-products" was also included in the search. Thus, the search equation used was "biofuel" OR "bioethanol" OR "biobutanol" AND ("fermentation" OR "fermentation by-products") AND "pervaporation". The number of publications on biobutanol has experienced exponential growth during the analyzed period, likely due to its technical advantages over bioethanol, including a higher energy content and lower volatility. The bibliometric analysis identified three fields of intense research: 1) optimization of the fermentation process, particularly the selection of appropriate substrates and conditions to increase efficiency in obtaining biobutanol; 2) development of separation technologies, pervaporation being the most prominent between 2014 and 2023; 3) understanding of the phenomenology involved in biofuel production, whether in fermentation or separation technologies; these key aspects have been addressed through scientific cooperation between the United States, China, and some European countries. In summary, there is a growing interest in conducting research into sustainable bioethanol and biobutanol production, with a particular focus on optimizing fermentation processes, improving separation technologies, and valorizing fermentation by-products. These advances reflect a continued commitment to biofuels development and the consolidation of a biorefinery-based approach.

Effect of Fermentation Broth Composition and Membrane Material on Pervaporation Performance

Some by-products of the fermentation process can influence pervaporation performance, impacting both the flux and separation factor. Furthermore, the addition of species, such as inorganic salts or microorganisms, can also modify flux and separation factor. Table 1 lists some species commonly present in fermentation broths and their effect on separation performance. Particularly, the presence of furfural and the addition of inorganic salts such as ammonium sulphate ($(NH_4)_2SO_4$) and calcium chloride ($CaCl_2$) have been shown to increase the flux and separation factor of alcohols, mainly in the production of bioethanol.

Membrane material is a critical factor in pervaporation performance, particularly in separation processes such as ethanol production. Polydimethylsiloxane (PDMS) is one of the most widely used membrane materials because of its high permeability to organic compounds, as well as its thermal and chemical resistance. To optimize its selectivity and performance in various applications, e.g., by reducing swelling in the presence of high ethanol concentrations and/or improving mechanical and thermal stability, bulk or surface modifications of PDMS membranes have been reported (Chen et al., 2014; Kanemoto et al., 2016). These modifications are summarized in Figure 2 and briefly discussed below.

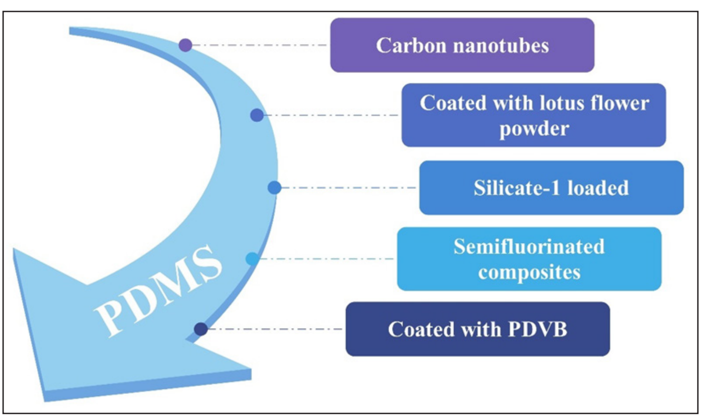

Figure 2. Polydimethylsiloxane (PDMS)-based membranes for bioethanol production
Note. PDVB = Polydivinylbenzene

Table 1
Effect of various species present in the fermentation broth on the performance of different membranes used in pervaporation

Membrane type	Species	Remarks	Reference
Silicalite-1-loaded PDMS	Furfural	Increase in ethanol flux. Furural is also permeable to PDMS membranes and can be recovered as a value-added product.	Cai et al. (2013) Chen et al. (2014) Gaykawad et al. (2013) Zhu et al. (2019)
	5-HMF	Decrease in water flux, ethanol flux not affected (ethanol production).	
	Vanilin	Decrease in ethanol flux, constant membrane selectivity (ethanol production).	
	4-hydroxybenzaldehyde	Decrease in total flux, reduction in water flux (ethanol production).	
	Catechol	Gradual decrease in total flux due to the obstruction by the oxidized form of catechol (benzoquinone).	
	Syringaldehyde	Decrease in total flux (ethanol production).	
	Acetic acid	Increase in water flux (butanol production).	
	Inorganic salts	Increase in flux, selectivity, and separation factor of bioalcohol (ethanol and butanol production) due to *salting-out*, which reduces the amount of free-water molecules and modifies the activity coefficients of the compounds in the feed.	
Silicate-1 coated with silicone rubber	Peptides (tryptone)	Decrease in total flux due to the zwitterionic nature of the peptides that reduces the hydrophobicity of the membrane.	Ikegami et al. (2014)
	Vitamins	If water-soluble, vitamins decrease selectivity and separation factor (butanol production) because of the reduction of the hydrophobicity of the membrane.	
Tubular silicate-1	Phenols	Decrease in total flux due to adsorption on porous silicate. The addition of activated carbon fixes this issue.	Kanemoto et al. (2016)
Silicate-1 loaded PDMS tubular silicate-1	Sugars	Increase in alcohol selectivity and decrease in total flux (ethanol production). Other sugars, such as glucose, increase the viscosity of the fermentation broth and resistance to ethanol transport, reducing its flux and partition factor. Sugars can also block the solvent diffusion pathways (e.g., zeolite channels).	Chen et al. (2014) Kanemoto et al. (2016)

Table 1 *(continue)*

Membrane type	Species	Remarks	Reference
PDMS Ceramics hollow fiber supported PDMS PET supported PDMS	Microorganisms	Effect depends on the membrane material: in silicate-loaded membranes, increase in alcohol flux with that of other components remaining constant by the addition of yeast (ethanol production); in PET (polyethylene terephthalate)-supported PDMS membranes, decrease in flux due to clogging of the membrane without effect on other membrane parameters.	Cai et al. (2016) Chen et al. (2014) Dong et al. (2014) Jaimes et al. (2021) Jung et al. (2018) Kaewkannetra et al. (2012)

Note. PDMS = Polydimethylsiloxane; 5-HMF = 5-hydroxymethylfurfural; PET = Polyethylene terephthalate

Incorporation of inorganic fillers such as nanoparticles or zeolites/silica into the PDMS matrix has been used to enhance the selective separation of larger organic molecules while preventing the transport of water. For instance, the addition of silicalite-1 into PDMS membranes improves the ethanol separation factor and reduces the flux (Chen et al., 2014; Santos et al., 2018) due to the hydrophobicity of silicalite and its preferential retention of ethanol, which prevents water permeation. However, above a certain threshold (saturation load), the ethanol flux decreases because of a reduction in the free volume of the membrane (Santos et al., 2018). Furthermore, silicalite-1-PDMS membranes would not be suitable for the separation of acetone, butanol, and ethanol (ABE) fermentation broth (especially butanol) because the acetic acid (fermentation by-product) decreases the selectivity by increasing water flux, as reported in Table 1 (Chen et al., 2014). It has also been documented that the incorporation of 10% CNTs in PDMS membranes increases the ethanol flux and the separation factor by 45.7 and 33.8, respectively (Xue, Wang, et al., 2016).

Other nanoscale effects have been exploited, such as the lotus effect, i.e., the ability of certain materials to repel water, analogous to how lotus leaves repel water due to their nanostructured surface (Xue, Wang, et al., 2016). For example, He et al. (2020) mixed PDMS with lotus flower powder to improve hydrophobicity, but the relatively large particles used created voids and defects in the membrane matrix, which compromised selectivity by allowing unwanted components to pass through, lessening membrane performance. Despite the drop in selectivity, the flux of the lotus flower powder-coated membrane increased by approximately 25% relative to the PDMS membrane, particularly when approximately 1.5 wt.% of lotus-flower powder was used.

Li et al. (2014) reported the use of a PDMS and polyacrylonitrile (PAN) membrane loaded with silicalitate-1 for the recovery of butanol from cassava-derived fermentation broths. The membrane achieved a separation factor between 29 and 32, with butanol flux ranging from 118.70 to 203.76 g/m^2 h. These results, comparable to those obtained with simulated models, suggest that the membrane did not experience fouling when used with the fermentation broth. Similarly to ethanol recovery, carbon nanotube modified membranes have also been used for butanol separation (Xue, Liu, et al., 2016).

F. Wang et al. (2024) employed slot coating to form vinyl-PDMS membranes on a porous support in as little as 20 min, achieving selective layers with tunable thicknesses from 0.4 to 15 μm. The resulting membrane exhibited a total flux of 2.8 kg/m^2 h and a separation factor of 10.3 when tested with a 5 wt.% ethanol/water mixture at 60°C. Furthermore, the authors reported that the incorporation of nanoparticles improved the permeability by up to 35% and increased the separation factor by approximately 15, allowing the membrane properties to be fine-tuned to specific process requirements.

On the other hand, the issue of compatibility between organic membranes and inorganic silicalite-1 particles needs to be considered, lest it negatively impacts the membrane selectivity. To this end, membranes incorporating metal-organic frameworks (MOFs), such as zeolitic imidazolate frameworks (ZIFs), have been proposed (S. Liu et al., 2013). The addition of this material in PDMS membranes improved the hydrophobicity and, therefore, increased the butanol separation factor, but organic acids present in the fermentation broth cause non-selective defects, such as interstices, which may significantly reduce the butanol separation factor and increase the flux. Si et al. (2019) reported that to avoid degradation, PDMS membranes were loaded with ZIF-derived carbon nanopores, which prevent membrane deterioration by organic acids and allow the membrane performance to match that observed with simulated models.

Chemical modification of the PDMS surface by introduction of functional groups has also been reported to augment the affinity for specific compounds, thus increasing the selectivity of the separation (Ikegami et al., 2014). Furthermore, blending PDMS with other polymers results in hybrid membranes with improved mechanical or selective properties according to the process requirements. Cross-linking, which involves the interconnection of PDMS chains, improves stability and resistance to swelling, allowing the membrane to perform better at higher ethanol concentrations (Chen et al., 2014).

Polydivinylbenzene (PDVB) coating has shown a 13% increase in the separation factor and a 30% increase in flux compared to the uncoated membrane. In addition, PDVB prevented the membrane from wetting and accelerated ethanol uptake. Semifluorinated self-assembled monolayer membranes with high hydrophobicity, prepared by ultraviolet (UV)/ozone photooxidation, have also been described. The fabrication conditions of membranes significantly influence their performance during pervaporation. Initially, a membrane operating at 60°C presented a high flux (412.9 g/m^2 h), but the separation factor was 13.1, suggesting a limited ability to effectively discriminate between the mixture components (ethanol and water). The membrane selectivity peaked with time-on-stream, with separation factors of 11.8, 13.1, and 9.7 at 30, 60, and 90 min, respectively, pointing to changes in the membrane structure or properties during the process (Li et al., 2013).

On the other hand, the properties of styrene-butadiene-styrene (SBS) membranes can be modified in the presence of a PDMS or polyurethane (PU) membrane (Santoro et al., 2017). When the SBS membrane is combined with a PU membrane, the flux increases due to the hydrophobicity of PU, while the selectivity improves when combined with a PDMS membrane. Both types of membranes showed increased flux as the feed ethanol concentration increased (from 3 to 9 wt.%), although their separation factor decreased. Optimal performance of these membranes was also achieved at 50°C and low ethanol concentrations (3 wt.%) to improve selectivity, or at high ethanol concentrations to promote flux (Santoro et al., 2017). In addition, the embodiment of self-assembled polystyrene block copolymer into PDMS membranes has attracted attention for its ability to improve membrane flux (increasing from 110 to 220 g/m^2 h), while achieving higher separation factors for acetone (7-fold increase) and butanol (3-fold increase) from a glucose-derived ABE fermentation broth (Shin et al., 2015).

Other materials different from PDMS have also been evaluated. Among them, polyvinyl alcohol (PVA) membranes coated with cellulose acetate are not attractive for implementation in the separation of alcohols from fermentation broths since the yields are reduced by up to 50% compared to simple aqueous solutions of 14.6% ethanol (Kaewkannetra et al., 2012). Polymer of mixed solvents (POMS) also showed poor performance, i.e., a permeate with an ethanol concentration between 1.5-1.8 wt.% when the concentration in the feed stream varied between 0.5-2.5 wt.% (Z. Zhang et al., 2021). POMS has also been used in separation membranes for butanol. Compared to PDMS membranes, a higher flux was achieved by using a fermentation broth derived from wheat straw, despite operating under conditions that led to a lower driving force; thus, for the POMS membrane, a pressure of 20 mbar and a temperature of 32°C were used, in comparison with 9-14 mbar and 37°C with PDMS. Similarly, the separation factor of the POMS membrane was higher than that of the PDMS membrane (Van Hecke & De Wever, 2017). Another polymer used for butanol separation in systems coupled to liquid-liquid extraction is sulfonated poly(arylene ether sulfone) (SPAES). This membrane provides a protective effect on the fermenting microorganisms against the solvent used in the extraction. Furthermore, it is noted that SPAES exhibited an intermediate affinity compared to membranes made with polyamide (PA) and PDMS (Kim et al., 2020). On the other hand, membranes made from polyetherimide (PEI) loaded with graphene oxide have been designed. The presence of epoxy, carboxyl, or hydroxyl functional groups of graphene oxide enhanced the diffusion of the feed mixture. PEI demonstrated a separation factor of 99.3, suggesting it as a promising membrane for butanol dehydration (Manshad et al., 2020).

The use of catalytically active membranes, which can immobilize the microorganisms responsible for fermentation, has also been reported. These membranes exhibited similar flux and separation factors to PDMS membranes (Cao et al., 2020). Promising results have been obtained with hydrophilic membranes specifically designed to remove water while enriching ethanol in the feed stream. However, in a simultaneous fermentation and pervaporation process, this approach could be problematic, as rapid water removal can hamper microbial activity essential for fermentation. Microorganisms, such as *Saccharomyces cerevisiae*, require water for growth and metabolism, and excessive water removal could limit ethanol production. Furthermore, high ethanol concentrations could become toxic to microorganisms, reducing fermentation yield, making it important to balance the ethanol concentration to achieve maximum process efficiency. Some of these membranes are made from PVA and graphene, where the latter creates nanochannels within the membrane matrix that host water monolayers. Increasing the loading of graphene improved the flux and selectivity towards water, while reducing the ethanol flux to almost zero (Kalahal et al., 2021). Similarly, high water permeability carbon molecular sieve membranes (CMSM) have been described, as well as other types of hydrophilic membranes developed by Rahimalimamaghani et al (2022). From these works, it was concluded that to attain a high ethanol concentration, membranes should be designed to achieve separation factors close to 10,000 when operating at 5% ethanol concentration in the feed stream (Nagy et al., 2015).

The incorporation of alkyl fluorinated groups has been reported to mask the clogging caused by the microorganisms in the fermentation broth, yielding a 37% increase in flux, a 104% increase in separation factor, and high stability during continuous butanol removal compared to membranes without alkyl fluorinated groups (Zhu et al., 2020).

Polyether-block-amide (PEBA) loaded with ZIF-71 metal-organic framework membranes has been reported for butanol pervaporation. The increased hydrophobicity of this structured network enhances the affinity of the membrane for butanol, influencing both the flux and separation factor, according to S. Liu et al. (2013), membrane flux and separation factor are maximized at 20 and 25% ZIF-71 (Figure 3) loadings, respectively, while a reduction in flux and separation factor was observed for acetone and ethanol present in the ABE fermentation broth.

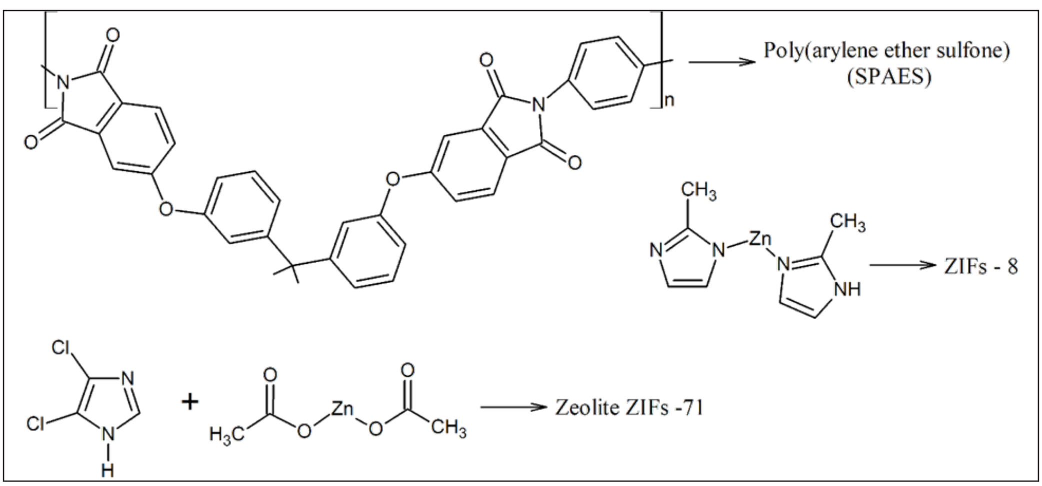

Figure 3. Membranes reported in biobutanol production
Note. SPAES = Poly(arylene ether sulfone); ZIF = Zeolitic imidazolate framework

Komal et al. (2024) investigated the need for efficient approaches to traditional butanol separation methods, which are costly and energy-intensive. In their study, a novel strategy was implemented using mixed-matrix membranes (MMMs) incorporating ZIF-8 in liquid form (ZIF-8-PL) into PDMS. Compared to conventional membranes (unmodified PDMS), membranes containing ZIF-8-PL showed significant performance improvement, achieving a ca. 102% increase in flux and a 15% improvement in separation factor, highlighting the advantages of ZIF-8. Therefore, MMMs with liquid fillings (PL) represent a promising approach to optimize energy efficiency and reduce costs in industrial-scale butanol separation.

Several ionic liquids have been proposed in combination with PVA and polytetrafluoroethylene (PTFE) membranes (Figure 4). It has been established that the presence of these ionic liquids increases the flux, particularly with 1,3,5-Tris(bromopropyl) benzene (TBP-Br), due to the high hydrophobicity and flexibility of the polymer chains, which expands the free volume of the membrane. However, the separation factor increased with higher loadings of 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene chloride (TBRDP-Cl) or 1,3,5-Tris(bromomethyl)benzene (TBMP), reaching a maximum value of 147 for the membrane with 30% 1,3,5-tris(bromomethyl)phenyl-functionalized mesoporous silica (TBMP-MS), while the opposite effect was observed with TBP-Br (Sajjad et al., 2019). Contrarily, it is necessary to use a gelling agent to prevent the leaching of other ionic liquids out of the membrane when working at low pressures, thus ensuring mechanical stability during operation, as was reported by Plaza et al. (2013) with the ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6) on a polytetrafluoroethylene (PTFE) membrane: the interaction with the membrane led to preferential transport of butanol, which was the cause of the higher partition coefficient.

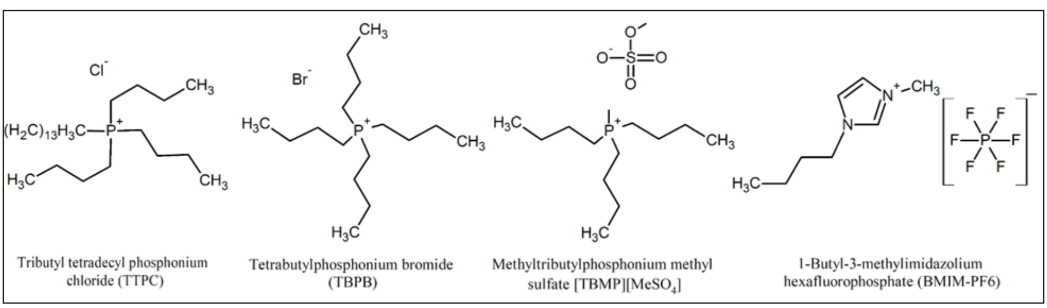

Figure 4. Ionic liquids used in polyvinyl alcohol and polytetrafluoroethylene membranes for butanol pervaporation

Approaches to Improve Pervaporation Performance

Depending on the type of fuel alcohol, a wide variety of bacterial strains and biomass have been studied for the fermentation processes, as shown in Figure 5. Bioethanol production has been reported from various sources, mainly those with high polysaccharide content that do not endanger food safety, such as wastes of banana (Wagner & Gasch, 2023), corn (Chen et al., 2014), newspaper (Trinh et al., 2013), coffee (Nguyen et al., 2017), or cruciferous vegetables (Song, Nguyen, et al., 2017), as well as non-waste sources such as Jerusalem artichoke (Song, Oh, et al., 2017), bamboo (Song et al., 2020), rye straw, and willow wood

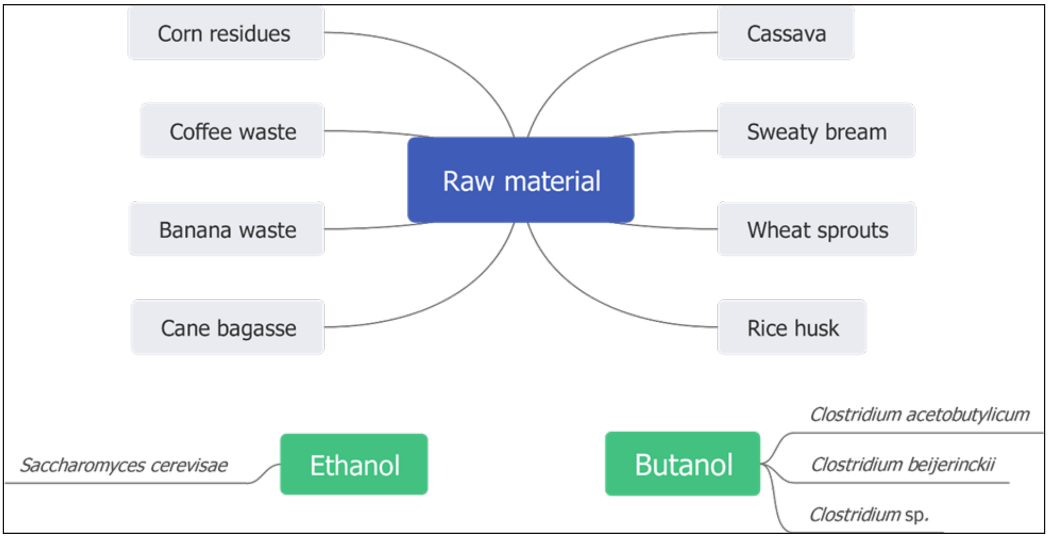

Figure 5. Sources and microorganisms are available to produce ethanol and butanol by pervaporation coupled with fermentation

chips (Gaykawad et al., 2013). The fermentation is mainly carried out by the *S. cerevisiae*. However, the use of other types of yeast has also been described, such as autoflocculants resulting from the fusion of protoplasts of *S. cerevisiae* and *Schizosaccharomyces pombe* strains (Xue, Wang, et al., 2016). The reduction of the complex sugars from these sources, required to carry out the fermentation and achieved by a previous stage of acid hydrolysis, is key to improving fermentation performance since microorganisms such as *Clostridium pasteurianum* or *S. cerevisiae* mainly metabolize simple sugars, such as glucose. Therefore, this stage must be carefully controlled to balance the higher amount of sugars obtained at higher acid concentrations with the concomitant formation of byproducts that could affect membrane performance (de Andrade et al., 2021).

It has also been proposed to use ionic liquids such as 1-butyl-3-methylimidazolium chloride combined with inorganic acids to dose the acid during hydrolysis (Trinh et al., 2019), increasing the production of fermentable sugars and, as a result, a higher ethanol yield in the fermentation broth and a higher ethanol concentration in the permeate. Additionally, yeast immobilization has been evaluated to improve ethanol productivity. For instance, Santos et al. (2018) reported that the use of calcium alginate to immobilize *S. cerevisiae* resulted in a 1.4-fold increase in ethanol concentration.

From a land use and agricultural efficiency perspective, bioethanol is a better option than biodiesel, as approximately 420 gallons/acre of ethanol can be produced compared to only 60 gallons/acre of biodiesel from soybeans. Furthermore, depending on the feedstock and process, soybean oil prices could increase with increased biodiesel production.

However, technical hurdles, such as corrosiveness, water miscibility, low energy density, and volatility losses, complex higher bioethanol blends. In contrast, *n*-butanol is a superior alternative fuel due to its higher heating value, and lower corrosiveness, polarity, volatility, and heat of vaporization, which minimize ignition problems in internal combustion engines. Furthermore, blends of butanol and petroleum-derived fuels may be used without engine modification. In addition, butanol produces lower carbon dioxide (CO_2), nitrogen oxide (NO_x), and sulphur oxides (SO_x) emissions compared to ethanol or gasoline. These advantages, coupled with the significant global demand for biofuels (approximately 51 billion gallons in 2022), are driving increased interest in the sustainable production of biomass and organic wastes, thereby reducing dependence on fossil fuels (Kanemoto et al., 2016; Lee & Lin, 2024).

Biobutanol production has been reported using a variety of bacterial strains to ferment materials derived from sweet sorghum (Cai et al., 2013; Kanemoto et al., 2016), wheat, sugarcane bagasse (Van Hecke & De Wever, 2017), and corn (C. Zhang et al., 2019, 2021) (Figure 5). Cassava has also been considered as a potential source of biobutanol due to its ability to grow in a variety of soils, thus avoiding competition with other crops (Li et al., 2014). Among the innovations in butanol production, the use of bacterial strains other than *Clostridium acetobutylicum* has been reported. Jung et al. (2018) documented the use of Enterobacter aerogenes to produce isobutanol, a biofuel alternative. In particular, about 83% of the isobutanol was recovered at concentrations ranging from 55 to 226 g/L using a PDMS membrane (Jung et al., 2018). The ability of *Clostridium* sp., on the other hand, to produce fuel-grade butanol without acetone as a by-product is very promising because it eliminates the need for an additional step to separate the butanol-acetone mixture (all membranes reported to date exhibit high affinity for both acetone and butanol) (Xin et al., 2016).

A feasibility study for obtaining butanol with *C. pasteurianum* GL11 demonstrates remarkable progress in the sustainable and cost-effective production of biofuels, making this strain an excellent candidate for industrial applications. In batch fermentation using glycerol, *C. pasteurianum* GL11 achieved a butanol concentration of 14.7 g/L with a yield of 0.41 g/g, while removing by-products such as acetone and 1,3-propanediol (1,3-PDO), which simplifies separation processes and improves productivity. Furthermore, when *in situ* extraction was applied during fed-batch fermentation, butanol reached 28.8 g/L, demonstrating the potential of integrating advanced extraction techniques to scale up production. Another key feature of *C. pasteurianum* GL11 is its ability to hydrolyze complex polysaccharides such as starch and xylan into butanol. This process is facilitated by the secretion of xylanases and amylases, allowing for consolidated bioprocessing that reduces the need for external enzymatic treatments and lowers substrate preparation costs. This combination of efficient substrate use, high productivity, and cost reduction positions

C. pasteurianum GL11 as a promising candidate for industrial-scale butanol production (Jung et al., 2018; Xin et al., 2016). Indeed, its ability to utilize low-cost substrates, such as glycerol (a biodiesel byproduct) and polysaccharides, as well as its high tolerance to butanol and optimized metabolic profile, reduces the energy demands of separation techniques, making the process economically viable and environmentally sustainable. Future research may focus on optimizing fermentation conditions and process scalability. Furthermore, co-fermentation with other renewable substrates can further diversify applications and improve productivity. This strain highlights the potential of combining genetic traits and innovative bioprocessing strategies to address global energy challenges while efficiently utilizing industrial waste streams (Xin et al., 2016).

Su et al. (2024)'s co-fermentation using dough and okara waste with *Clostridium* sp. strain BOH3 showed notable improvements in biobutanol production compared to individual fermentation. Using 80 g/L of a co-substrate composed of 85% mash and 15% okara, 15.9 ± 0.90 g/L of butanol and 25.4 ± 1.43 g/L of total solvents (acetone-butanol-ethanol) were achieved. These results represent increases of 91.6% in butanol and 108.2% in total solvents compared to the mash-only fermentation. The okara-only fermentation resulted in minimal solvent production due to its unfavorable carbon-to-nitrogen ratio. Furthermore, cofermentation accelerated 1.7-fold the transition from acidogenesis to solventogenesis and increased enzyme activity (amylase and butanol dehydrogenase). These findings highlight cofermentation as an effective strategy to optimize the conversion of food waste into biobutanol sustainably.

Fermentation-pervaporation systems can operate under batch, fed-batch, and continuous conditions. Although the mode of operation does not directly influence the butanol concentration in the permeate, since the mass transfer mechanism through the membrane is not modified (unless the membrane itself is changed) (Cai et al., 2016; Fu et al., 2016; H. Zhang et al., 2023; L. Liu et al., 2021; Li et al., 2014; Shin et al., 2015) continuous removal of butanol ensures a higher fuel yield due to the mitigation of butanol-induced bacterial toxicity. Fractional condensation coupled to vapor compression and PDMS membranes has been explored to replace conventional condensation at low temperatures, resulting in the production of high-concentration ethanol (50%) with a selectivity of 20 and energy savings of up to 50% (Z. Wang et al., 2023). Stripping has also been employed as a pretreatment operation prior to pervaporation to remove butanol and other substances that could affect the membrane flux due to fouling, achieving high fuel concentrations, i.e., 44.7 g/L (Xue, Liu, et al., 2016) and 55.9 g/L (Rochón et al., 2020).

Challenges and Opportunities

In addition to the production of biofuels, the simultaneous fermentation-pervaporation process has also been used for the production of other valuable products. Mannose (a sugar) can be obtained from lignocellulosic biomass such as coffee grounds, reaching a purity of 95.3% (Nguyen et al., 2017). Psicose, an epimer of fructose, is obtained from inulin present in cruciferous plant wastes (Song, Nguyen, et al., 2017) and Jerusalem artichoke (Song, Oh, et al., 2017), and which has the potential to suppress hepatic lipogenic enzymes, has been produced together with ethanol using the strain *S. cerevisiae*. Xylose, which can be made from the fermentation of bamboo pretreated with hydrogen peroxide and acetic acid in the presence of *S. cerevisiae* and that, like psicose, cannot be metabolized by this yeast to ethanol, was obtained with high yield (89.6%, retentate stream) along with ethanol (82.6%, permeate stream) using PVA membranes. Furthermore, given the high availability of carbohydrates, this strategy could reduce water consumption up to 2.5 times per kilogram of ethanol obtained (Van Hecke et al., 2016).

Other approaches to reduce effluents have been reported by C. Zhang et al. (2019, 2021), who used the retentate as a buffer and nutrient source for the fermentation process, achieving savings of 86 to 92% in the feed stream and recovering 94% of ABE from the fermentation of corn residues with *C. acetobutylicum*. Despite the presence of acids that can be toxic to microorganisms during fermentation, no significant deleterious effect was observed because of the conversion of acids into lipids by using *Rhodotorula glutinis*.

While Outram et al. reported improvements in fermentation yield of up to 67% (Outram et al., 2017), Xue, Wang, et al. (2016) reached ethanol concentrations of 615.1 g/L in the permeate with CNT/PDMS membranes. Furthermore, using a zeolite-PDMS membrane, they achieved 253 g ABE/L in the condensate (Xue et al., 2015). This represents an increase in ethanol concentration from 3 to 4% compared to conventional fermentations, with a maximum ethanol purity in the permeate of 78%. Similarly, in ABE fermentation combined with pervaporation, ethanol purity in the permeate ranges from 2 to 27%. These findings suggest that hybrid membranes can significantly reduce energy consumption in the recovery of biobutanol and bioethanol. Currently, pervaporation membranes are limited to laboratory-scale development, facing challenges in scalability, cost optimization, and integration with fermentation processes. Key issues include improving durability, stability, and long-term performance. Overcoming these challenges is essential to establishing pervaporation as an efficient, stable, and cost-effective solution for biobutanol and bioethanol production.

CONCLUSION AND FUTURE PERSPECTIVES

Pervaporation separation is a highly efficient operation for the recovery of organic solvents, particularly alcohols derived from fermentation processes. The integration of pervaporation and fermentation creates a system of great interest to produce biofuels, mainly bioethanol and biobutanol. To improve pervaporation performance and achieve high biofuel yield and purity, it is common practice to tune both the alcohol concentration in the fermentation broth (liquid feed stream) and the operating temperature of the pervaporation process. While these are the most common factors evaluated, they are not the only ones that influence the overall performance of the pervaporation-fermentation system.

The presence of furfural from biomass fermentation or added intentionally, as well as the addition of inorganic salts to the fermentation broth, contributes to improving flux and selectivity. The type of membrane material can also influence the performance of the fermentation-pervaporation system. The performance of PDMS membranes can be further improved by incorporating functional groups (amino, carboxyl, or sulfonyl) or species such as glycerol and sorbitol. In addition, loading of nanomaterials such as graphene, silicon nanocomposites, or carbon nanotubes can also improve the separation.

It is necessary to devise alternative polymers to PDMS that present a high affinity for alcohols, which can be achieved by establishing the chemical structure that optimizes the interaction of the alcohol with the membrane under specific conditions. Increasing the concentration of fermentable sugars during biomass pretreatment (hydrolysis) is another variable that inherently improves pervaporation performance, as it leads to higher biofuel concentrations in the fermentation broth.

From a different perspective, the use of strains, such as *Zymomonas mobilis* or *Bacillus subtilis*, can be advantageous as it allows the production of the desired biofuel while minimizing the generation of other solvents, such as acetic acid, butyric acid, ethers, and aldehydes. In addition to fermentation, integrating operations such as distillation, extraction, adsorption, crystallization, filtration, and ion exchange with pervaporation can optimize process performance. These ancillary techniques not only improve product purity and recovery but can also achieve energy savings of up to 50%. By combining these methodologies, the overall efficiency of biofuel production would be maximized.

In summary, pervaporation has gained increasing interest and importance as a separation method for biofuel production due to its dual capacity to produce value-added sugars and reduce the amount of raw material required for large-scale biofuel production. Therefore, research into new materials, genetic modifications of microorganisms, and development and implementation of additional operational processes are key points in the field of biofuel production by fermentation and pervaporation.

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