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Review on Membrane Materials for Ethanol/Water Separation by Pervaporation

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ABSTRACT

Bioethanol is produced through the fermentation of biomass. It has garnered significant research attention due to its potential as the next generation of sustainable energy. The fermentation broth must be purified before it can be used. This article reviews membrane materials for the separation of ethanol and water using pervaporation membranes. It covers the pervaporation mechanism, membranes for ethanol dehydration, membranes for ethanol recovery, and the prospects of using membranes in this application.

Keywords: Ethanol, pervaporation, membrane, polymer, inorganic

1.0 INTRODUCTION

Given the rapid depletion of fossil fuels, bioethanol has emerged as a compelling biofuel to meet the growing demand for fuel. Bioethanol's versatility in being blended with gasoline to create gasohol fuel makes it an especially attractive option [1]. Researchers have extensively studied bioethanol production, purification, and utilization. The number of academic articles published in the ScienceDirect database with the keyword 'ethanol-water separation' has shown an exponential increase from 2000 to 2022, as seen in Figure 1. Application of membrane material for ethanol and water separation by pervaporation is presented in this article.

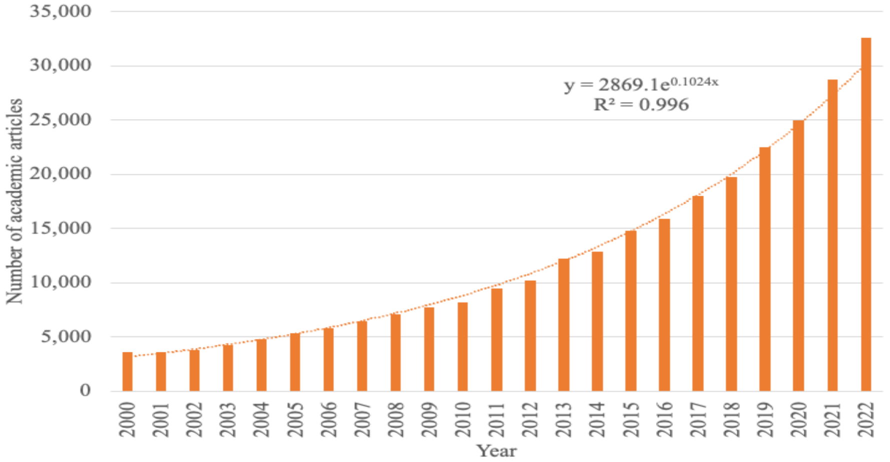

Figure 1 Number of academic articles for research on ethanol and water separation

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Bioethanol is produced through the fermentation of biomass, including sugars, corn, cellulosic biomass [2], and starches, by microorganisms such as yeast [3]. During fermentation, ethanol concentration increases with time, but the microorganisms used for fermentation cannot survive when the ethanol concentration exceeds 6-10 wt.% [4], depending on the specific microorganism. To produce fuel-grade anhydrous ethanol from fermentation, the water content must be reduced from around 85 wt% to less than 1 wt% [5]. Therefore, it is essential to remove ethanol from the fermentation broth to prevent the activity loss of microorganisms.

The process of separating ethanol from the fermentation broth is known as ethanol recovery. Another application of membranes in the production of bioethanol is ethanol dehydration, which involves removing water from a high ethanol concentration solution. This process yields high-purity ethanol suitable for various applications, including fuel, industrial processes, and laboratory use.

The conventional technique to concentrate fermentation broths is distillation. [4]. Distillation in energy intensive process and the alternative technology of pervaporation has potential to achieve the high ethanol concentration without using high energy consumption [6]. Pervaporation (PV) is a membrane technology used for the separation of liquid mixtures containing azeotrope components and close boiling mixtures, such as ethanol and water, through a dense membrane. It primarily serves the purpose of separating liquid mixtures and combines the principles of membrane permeation and evaporation. The performance of ethanol/water separation depends significantly on operating conditions and membrane materials. This paper will review various materials that have been developed or employed for the separation of ethanol and water mixtures through pervaporation.

2.0 MECHANISM

Pervaporation is a membrane process that combines both permeation and evaporation mechanisms into one process. It is primarily used for separating liquid mixtures, especially azeotrope mixtures. In this process, a liquid mixture is introduced to the feed side of the membrane, while the permeate side is maintained under vacuum conditions. The schematic diagram of the pervaporation process is shown in Figure 1.

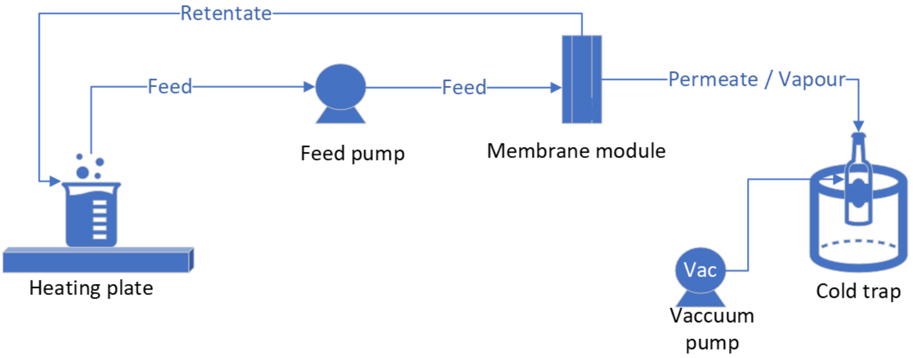

Figure 1 Schematic diagram of pervaporation process

To date, no process model can completely characterize every detail of mass transfer in membranes [7]. Figure 2 shows the solution-diffusion model for pervaporation mechanisms which involves (a) sorption of components on membrane surface, (b) diffusion of the components through membrane and (c) vaporization of desorption of components on the permeate side of membrane [8]. On the feed side, the liquid mixture is in contact with a selective layer, allowing the component to dissolve and adsorb onto the membrane surface. These adsorbed components accumulate on the membrane and then diffuse through it to the other side (permeate side). The permeation rate is higher for the more permeable component, which can readily pass through the membrane due to its close affinity to the membrane. Subsequently, the diffused component reaches the other side of the membrane and experiences vacuum or low-pressure conditions, causing its transition from a liquid to a vapor phase through vaporization. The vaporized component is then condensed in a cold trap and collected as the final product. The remaining liquid mixture, known as the retentate, is returned to the feed solution.

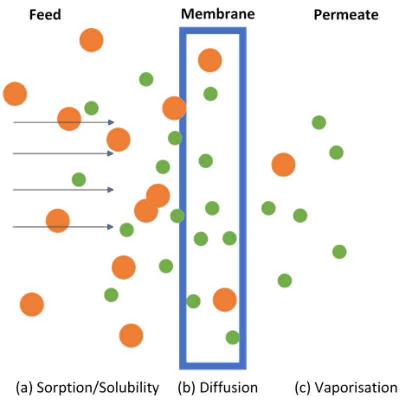

Figure 2 Pervaporation mechanism

The solution-diffusion model is applicable to both ethanol dehydration and recovery. In ethanol dehydration, the permeate consists of water, while in ethanol recovery, it's ethanol. Pervaporation is suitable for applications in separating azeotropic mixtures with close boiling points and removing water from organic solvents, separating versatile compounds to create the concentrated solution.

Pervaporation efficiency can be assessed using various indicators like permeation flux and selectivity. Permeation flux depends significantly on membrane properties, including thickness, chemical affinity [9], and operating conditions [7]. Implication of the membrane properties on the performance is presented in the following section.

3.0 MEMBRANE PROPERTIES

Membrane characteristics influence its properties in which significantly impact on the separation process performance. This article addresses key properties such as hydrophilicity/hydrophobicity, permeability, separation factor, pervaporation separation index, and swelling.

Hydrophilicity/Hydrophobicity

Hydrophilicity refers to the degree of affinity of membrane materials for water, while hydrophobicity is the opposite. Hydrophilicity and hydrophobicity are typically determined through contact angle measurements. A surface is hydrophobic when its static water contact angle (θ) is greater than 90° and it is hydrophilic when θ is less than 90° [10].

Hydrophilic membranes typically exhibit high water perm-selectivity and are effective at removing water from the feed stream. In any membrane separation process, it is both technically and economically suitable to remove a minor component from the feed stream. In the case of ethanol dehydration, water is considered a minor component, making hydrophilic membranes the recommended choice. Pervaporation with hydrophilic membranes is also well-suited for the dehydration of various organic compounds in industrial processes.

On the other hand, for the ethanol/water separation process in a low ethanol concentration feed, where ethanol is the minor component, it's advisable to use an ethanol perm-selective membrane or a highly hydrophobic membrane. Such membranes selectively transport ethanol through them.

Permeability, Separation Factor, Pervaporation Separation Index

Pervaporation flux (J, g/m^{2}h) is one of the measurements for membrane performance, taking permeate quantity, membrane surface area and separation duration into account. Different membrane preparation techniques can lead to various membrane characteristics, including thickness. While membrane thickness provides mechanical strength, it can also increase diffusion resistance and reduce the quantity of permeate.

To account for the effect of membrane thickness (D, m) on pervaporation flux (J, g/m^{2}h) when comparing membrane performance, permeability (P, g/mh) instead of flux (J, g/m^{2}h) is used. The permeability is defined in Equation (1):

$$P = J\,D \tag{1}$$

Generally, the higher the permeability indicates higher efficiency of the membrane. However, in most cases permeability is inversely proportional to selectivity thus the overall separation performance of the membrane should be evaluated together with separation factor.

Separation factor (β, −) is another measurement of the pervaporation membrane performance. A high separation factor is desired as it indicates that the membrane can effectively separate the desired components from the feed stream. Separation factor (β, −) is determined from Equation (2):

$$\beta = \frac{(\frac{x_{EtOH}}{x_{water}})_{permeate}}{(\frac{x_{EtOH}}{x_{water}})_{feed}} \tag{2}$$

where x_{EtOH} is the weight fraction of ethanol and x_{water} is the weight fraction of water. Together with permeability or flux, these two characteristics are key points to determine the overall pervaporation membrane performance. The overall separation performance is represented by the pervaporation separation index (PSI, g/m^{2}h) defined [11] by Equation (3):

$$PSI = J(\beta - 1) \tag{3}$$

PSI parameter is used to compare separation effectiveness of membranes possessing different separation and transport properties [12]. From the aspect of energy consumption, the separation factor of pervaporation membranes must be larger than 20 to compete with distillation [13].

Swelling and Other Properties

Ethanol/water mixtures can have different swelling effects on a membrane. Swelling tests are essential to evaluate material compatibility with the swelling solvent, ensuring long-term stability and performance. The selection of the swelling solution or sometimes called the target solution is important, normally the target solution is the expected feed solution in pervaporation. For instance, 5% ethanol solution and water were the target solutions for swelling tests of silicalite-1/PDMS composite membrane prepared for ethanol recovery from fermented santol broth [8]. It's crucial to control and optimize the swelling degree for efficient separation, as excessive swelling can reduce membrane selectivity.

Desirable properties of membrane materials also include high chemical resistance, thermal resistance, and stable mechanical strength when exposed to the target solution. Additionally, material cost and processability are important factors to consider. Manufacturing cost is crucial for commercial viability, while processability plays a key role in the convenient design of pervaporation systems.

4.0 MEMBRANE MATERIALS

Pervaporation membrane performance relies on membrane material characteristics, specifically their solubility and diffusivity selectivities. Hydrophilic membranes demonstrate strong solubility selectivity for water molecules over ethanol. Consequently, water molecules are absorbed on the feed side of the membrane surface and are available for diffusion to the permeation side. This process, involving the separation of water from a water/ethanol feed solution using a hydrophilic membrane, is commonly known as ethanol dehydration.

Ethanol recovery via hydrophobic membrane pervaporation involves separating ethanol from a dilute water/ethanol feed mixture [8]. In this process, a hydrophobic membrane selectively adsorbs ethanol over water due to differences in affinity with the membrane material. As the feed solution contacts the membrane, ethanol molecules preferentially adsorb onto the membrane and then diffuse through it to the permeate side. This hydrophobic membrane pervaporation method is valuable for enhancing ethanol purity for various applications.

This study evaluates membrane materials for ethanol dehydration and ethanol recovery independently in order to facilitate the reader's understanding. Table 1 and Table 2 are summary of membrane performance in ethanol dehydration and ethanol recovery, respectively.

Polymeric and Mixed Matric Membrane for Ethanol Dehydration

The commonly studied membranes for ethanol dehydration research are poly(vinyl alcohol), chitosan, alginate and polyimide. Information of these membranes and a few others are presented.

Poly(vinyl alcohol) (PVA)

Poly(vinyl alcohol) or PVA films are known for their high-abrasion resistance, elongation, tensile strength, and flexibility, and they have found applications in various commercial membranes. According to the solution-diffusion model, both water and ethanol molecules dissolve at the membrane's feed side surface and then diffuse towards the permeation side of the PVA membrane driven by the concentration gradient. PVA is a hydrophilic polymer [14] whose hydroxyl groups have strong interactions with water through hydrogen bonding, thus it owns excellent water perm-selective properties. Water molecules exhibit a stronger affinity for the PVA membrane compared to ethanol molecules, causing them to preferentially dissolve and migrate to the permeation side. This selectivity contributes to the dehydration of ethanol on the feed side [15]. PVA membranes are among the limited high molecular weight water soluble resins and can be readily cross-linked either chemically or thermally. Most research on PVA-based membranes has focused on chemical modifications to enhance perm-selectivity and stability.

Chitosan (CS)

Chitosan, a linear polymer comprising primarily of glucosamine exhibits high water perm-selectivity and solvent stability. It is soluble in aqueous acidic media via primary amine protonation. It is abundant in nature and is versatile for various applications due to its wide variety, low cost, thermal stability, and excellent film-forming properties [16]. It is another promising membrane material for ethanol dehydration. The polar groups on the chitosan membrane surface absorb water molecules [17] and transport them through the membrane thickness to the permeate side [18]. Many chitosan membranes show superior separation performance to cross-linked PVA membranes on ethanol dehydration [19]–[21]. Examples of membrane performance are listed in Table 1. Furthermore, with the aid of reactive hydroxyl and amino groups, chitosan can be further modified to suit specific pervaporation applications.

Alginate (Alg)

Alginate, a hydrophilic polysaccharide polymer, has gained attention as a membrane material due to its high flux and separation factor among hydrophilic materials. Research focuses on alginate membranes in combination with sodium ions (Na+) as their counter ion [22], [23]. Recent developments have integrated alginate and chitosan membranes. In general, alginate membranes demonstrate better separation performance, while chitosan membranes typically exhibit higher flux [24].

Composite alginate membranes filled with chitosan (phosphorylated, glycidol, or glutaraldehyde crosslinked) have been studied. Alginate membranes filled with phosphorylated chitosan particles at 10 wt% gave the best results, for which separation factor, flux and PSI were equal to 136.2, 1.90 kg m^{-2} h^{-1} and 256.9 kg m^{-2} h^{-1}, respectively.

Researchers have prepared a new concept of applying magnetic power to polymer. The composite alginate membranes were filled with hard magnets in the form of a Magnequench fine powder (MQFP) for highly efficient ethanol dehydration. The alginate membrane filled with 1 wt% of MQFP powder with the grains size of 15 μm showed the highest value of separation factor up to 12271 [25].

Polyimide (PI)

Ethanol dehydration with a hydrophilic membrane is successful because the membrane enhances both the solubility and diffusivity of water, which has a smaller molecular size compared to ethanol [26]. Polyimide is known for its excellent thermal, chemical, and mechanical stabilities [27]. Referring to the solution-diffusion model, the interaction between the permeating liquid (ethanol solution) and the functional groups of the polymeric membrane influences the sorption step. Polyimide membrane material exhibits selectivity toward water over ethanol molecules [28]. Polyimide membranes' selectivity for water is attributed to their rigid chemical structure with a high glass-transition temperature and the preferential interaction between water molecules and the imide groups through hydrogen bonding [28]. Dissolved water molecules on the membrane surface then diffuse through the polyimide material to the permeate side before evaporating as vapor downstream of the membrane. In this regard, the selection of aromatic monomers (dianhydrides and diamines) for polyimide synthesis is crucial for structuring its chemical composition and properties to achieve the desired membrane separation.

Others

Several other membrane materials have been studied for their pervaporation performance in ethanol dehydration, including polyacrylic acid (PAA), polyacrylonitrile (PAN), cellulose sulfate, and others. Recently, there has been research on the integration of PVA and PVA-alumina silicate ($Al_2O_3 \cdot SiO_2$) as selective layers for PAN membranes in ethanol dehydration [29]. Membrane fluxes decreased with addition of $Al_2O_3 \cdot SiO_2$ nanoparticles to the selective layer due to the increase in selective layer thickness. However, ethanol/water separation factor increased significantly with the enhanced membrane hydrophilicity [29].

Table 1 presents the pervaporation performance of membranes for ethanol dehydration. Among the numerous variables, one of the critical ones is the membrane material, which affects the performance indicators (e.g., flux and separation factor). In most cases, membranes exhibit a trade-off relationship; they either show an improved separation factor with a significantly reduced flux or an enhanced flux with a lowered selectivity

Table 1 Pervaporation performance of membranes for ethanol dehydration

Membrane	**Ethanol concentration in feed (wt%)**	**Temperature (°C)**	**Flux (g/m^2h)**	**Separation factor (-)**	**Reference**
PVA	85	50	42	40.2	[30]
PVA/7 wt% sulphosuccinic acid	90	70	300	175	[31]
PVA/7 wt% sulphosuccinic acid	90	60	180	240	[31]
PVA/5 wt% Li+ sulphosuccinate	90	50	59	44	[32]
PVA/glutaraldehyde	96	40	279	107	[33]
Pristine PVA	95.4	75	247	721	[34]
PVA	96	60	120	10	[35]
PVA/sericin blend	91.5	50	70	90	[36]
Chitosan	90	80	54.18	158.02	[21]
Chitosan/ H-ZSM-5 8wt% where Si/Al = 50	90	80	230	152.82	[21]
Chitosan/ 0.1 ml of absolute ethanol	96		3,534	599.7	[37]
α-alumina support with a 3 wt.% chitosan	90	60	352	200	[20]
Chitosan	95	24	120	2.4	[38]
Chitosan/bacterial cellulose	95	24	214	9.2	[38]

Membrane	**Ethanol concentration in feed (wt%)**	**Temperature (°C)**	**Flux (g/m^2h)**	**Separation factor (-)**	**Reference**
Sodium alginate	90	60	210	11,600	[39]
Sodium alginate/PVA blend	90	45	380	380	[40]
Alginate/phosphorylated chitosan microparticle membranes at 10 wt%	96	20	1,900	136.2	[24]
Membrane	Ethanol concentration in feed (wt%)	Temperature (°C)	Flux (g/m^2h)	Separation factor (-)	Reference
Sodium alginate - mMXene	90	70	505	9946	[41]
Pure sodium alginate	90	70	669	929.3	[41]
Polyimide with asymmetric polysulfone	90	40	1,700	240	[42]
Polyimide with asymmetric polyimide	94	30	200	800	[43]
Polyimide (HXDA)	90	150	1,700	240	[42]
Pure PI	90	42	240	260	[44]
ZIF-8/ PI MMS	90	42	260	300	[44]
0.53 mm silica sphere/PI MMS	90	42	310	190	[44]

Polymeric and Mixed Matric Membranes for Ethanol Recovery

Since the 1980s, several membrane materials ranging from polymeric, inorganic and mixed matrix membranes (MMMs) have been extensively investigated. Examples of the commonly studied membranes for ethanol dehydration research are poly(dimethylsiloxane), poly[1-(trimethylsilyl)-1-propyne] and styrene. Information of these membranes and a few others are presented.

Poly(dimethylsiloxane) (PDMS)

Poly(dimethylsiloxane), often referred to as "silicone rubber", is the most widely studied as a membrane material for bioalcohol recovery due to its hydrophobic nature [45]. PDMS is also effective in removing acetone, butanol, and ethanol from binary and quaternary aqueous mixtures [12]. PDMS membranes exhibit ethanol separation factors in the range of 4–15. Variation in membrane selectivity and flux in PDMS membranes are influenced by factors such as starting materials, membrane casting method, cross-linking degree, membrane module design, and testing conditions.

PDMS composite membranes consist of a PDMS thin film layer coated on a porous support to enhance flux. The supporting porous material also significantly influences both flux and membrane selectivity. The following commercial hydrophobic membranes are commonly used: Pervatech PAN-PV (Pervatech, the Netherlands), PERVAP-1060 and PERVAP-1070 (Sulzer, Chemtech, Switzerland). All membranes are PDMS based composite membranes, however PERVAP-1070 is additionally filled with ZSM-5 hydrophobic zeolite [12], [46]. A report shows that membranes consisting of a thin PDMS layer deposited on ZrO_2/Al_2O_3 porous ceramic supports displayed a remarkable total flux up to 19,500 g/m^{2}h and a separation factor of 5.7 for 4.3 wt% ethanol feed solution at 70 °C [47].

The reported ethanol–water separation factor for "pure" silicone rubber membranes ranges from 4.4 to 14.4 with an average of about 7–8 [8], [46]. To improve selectivity toward ethanol, hydrophobic fillers are cooperated with polymeric membranes, creating mixed matrix membranes (MMMs). For example, silicalite-1 was synthesized by controlling the gel molar composition in hydrothermal synthesis before being incorporated into a polydimethylsiloxane (PDMS) membrane on a Teflon support. These membranes were used for pervaporation of santol fermented broth. MMMs with 20 wt% silicalite-1 improved the separation factor in broth from 2.55 to 5.56. The overall pervaporation separation index with a santol broth of the 20 wt% silicalite-1/PDMS and commercial PDMS membranes were 2199 and 2110. [8]

High-silica ZSM-5 zeolites were incorporated into poly(dimethyl siloxane) (PDMS) polymers to form mixed matrix membranes for ethanol removal from water via pervaporation. Membrane formulation and preparation parameters were varied to determine the effect on pervaporation performance including siloxane chain length, crosslinking agent concentration and density of reactive groups, catalyst level, solvent type, zeolite type and loading, mixing method, and presence of a porous support membrane. The highest observed selectivity of 3.0 was observed with 65 wt% zeolite loading, [46]. Zhan *et al*. further modified ZSM-5 zeolite by etching it with HF acid and the MMM made of PDMS and this treated zeolite gave better flux and selectivity than the untreated zeolite filled PDMS membrane for the same ethanol–water mixtures [48].

Poly[1-(trimethylsilyl)-1-propyne] (PTMSP)

In the search for a substitute for PDMS membranes, researchers have explored PTMSP membranes, a glassy polymer with a large free volume. PTMSP membranes have demonstrated significantly higher flux (3 times) and a 2-fold increase in concentration factor compared to PDMS membranes [49]. The ethanol/water separation factor of PTMSP membranes falls in the range from 9 to 20 (see Table 2). Overall, PTMSP membranes exhibit greater membrane selectivity and flux relative to conventional PDMS membranes under similar operation conditions. However, the separation performance of PTMSP membrane is not very stable and declines as a function of time probably due to the compaction of the polymer and/or the sorption of foulants within the membrane.

Styrene

Polystyrene thermoplastic is naturally hydrophobic, but pure polystyrene plastic membranes tend to be brittle. Researchers have addressed this issue by blending polystyrene with other polymers to enhance its mechanical properties. For instance, one group chose for poly(butyl acrylate) rubber, known for its softness but lack of mechanical stability, and created a copolymer by adding fillers such as nanoclay [50]. These membranes were tested for ethanol recovery of 2.5–15 wt% ethanol solution pervaporation. The mixed matrix copolymer membrane containing 2% (wt% of total polymer) clay yielded the best result with a flux of 340 g/m^2 h and an ethanol selectivity of 26.4 at 30 °C for 5 wt% ethanol in water was observed.

Others

Table 2 presents literature data on the pervaporation performance of membranes for ethanol recovery, including PDMS, PTMSP, styrene, and other materials. Research has aimed to identify alternative materials to replace PDMS and PTMSP, but the reported options are limited. These alternatives include styrene-fluoroalkyl acrylate graft copolymers, polyorganophosphazene, styrene-butadiene-styrene block copolymers, polyurethane, polyurethaneurea, poly(ether-b-amide) or PEBA [51], Polyvinylidene fluorideor PVDF [48], fluorinated polyimides and others. However, only a few of these alternatives show promise for replacing PDMS and PTMSP.

For instance, Ishihara and Matsui (1987) reported that membranes fabricated using a styrene-fluoroalkyl acrylate graft copolymer on a cross-linked PDMS support displayed an excellent ethanol/water separation factor of 46, which is significantly higher than the intrinsic PDMS separation factor of 11 [52]. Recently, Ghofar and Kokugan (2004) investigated the pervaporation characteristics of microporous polytetrafluroethylene (PTFE) and polypropylene (PP) membranes for ethanol-water separation. They found that the resulting membranes are ethanol perm-selective and the ethanol-water separation factor could reach as high as 75 at an optimal downstream pressure conditions [53].

Table 2 Pervaporation performance of membranes for ethanol recovery

Membrane	**Ethanol concentration in feed (wt%)**	**Temperature (°C)**	**Flux (g/m^2h)**	**Separation factor (-)**	**Reference**
PDMS/silicalite (60 wt%)	5	50	105	21	[54]
PDMS/silicalite-1 (40 wt%)	5	50	60	17.9	[55]
PDMS/silicalite-1 (30 wt%)	6	40	51	14.9	[56]
PDMS/hollow sphere silicalite-1 shell (30 wt%)	6	40	72	15.3	[56]
PDMS on PTFE /silicalite-1 (30 wt%)	5	50	39	13	[57]
F-PBZ modified PDMS on PTFE /silicalite-1 (30 wt%)	5	50	207	28.7	[57]
PDMS on PVDF /HF etched ZSM-5 (30 wt%)	5	50	134	16.7	[48]
PDMS/silicalite-1 (20 wt%)	10	45	597	3.14	[8]
PDMS/ZIF-71 (40 wt%)	2	60	55,470 barrer*	12.5	[58]
PDMS/POSS (5 wt%)	10	50	536	17.7	[59]
PTMSP/PAF-1 (10 wt%)	10	40	247	12.7	[60]

Membrane	**Ethanol concentration in feed (wt%)**	**Temperature (°C)**	**Flux (g/m^2h)**	**Separation factor (-)**	**Reference**
PTMSP/p-DCX (10 wt%)	10	40	341	13.7	[60]
Membrane	Ethanol concentration in feed (wt%)	Temperature (°C)	Flux (g/m^2h)	Separation factor (-)	Reference
Poly(styrene-co-butylacrylate) copolymer/ nano clay (Cloisite 15A) (2 wt. %)	5	30	340	26.4	[50]
PEBA on PAN /silicalite (2 wt5%)	5	40	833	3.6	[61]
PEBA 2533/POSS (2 wt%)	5	65	427	5.7	[51]
PDMS layer deposited on ZrO_2/Al_2O_3 porous ceramic supports	4.3	70	19,500	5.7	[47]

*Note that 1 barrer = $1x10^{-10}$ cm^3(STP) cm cm^{-2} s^{-1} $cmHg^{-1}$

Inorganic Pervaporation Membranes Materials

The common disadvantages of polymeric membranes are poor swelling resistance, low chemical and thermal stability, and especially the intrinsic trade-off effect between permeability and selectivity [62].

Inorganic membranes are not subjected to any solvent induced swelling and have greater selectivity and flux than most polymeric membranes. Inorganic membranes such as silica and zeolite are thermally and mechanically stable. Their homogeneous structure and pore framework enable effective molecular sieving, resulting in reasonable permeation rates for transporting molecules.

Silica membranes can be prepared via sol–gel routes or chemical vapor deposition (CVD) methods on porous substrates for gas or pervaporation separation. Amorphous silica and A-type zeolite can be developed for ethanol dehydration of ethanol [63].

Zeolites are another widely studied pervaporation membrane material due to its unique pore structure, adsorption properties, and good mechanical, chemical resistance, and thermal stabilities. They are alumino-silicates with varied SiO_2/Al_2O_3 ratio and can form polycrystalline structure with well-defined nano-sized pores. They can be either hydrophobic at a high aluminium-to-silicon ratio to use for organic recovery, or hydrophilic at low aluminium to silicon ratio for dehydration application [64].

Despite so many advantages, the high cost and low processibility of inorganic materials limit their applications in membrane separation. It has been reported that the inorganic membranes of zeolite and 1-silicalite produced the separation factor of over 20 but they posed problems in processability of large-sized membranes, and they are often expensive [4]. Another example of inorganic membrane degradation happened to zeolite membrane application. Pure silica MFI zeolite membranes have the potential to separate ethanol/water mixture but its performance decrease with time due to formation of silanol groups in alkaline media. Researchers incorporated tungsten in MFI framework to prevent the formation. For 5 wt% ethanol solution, the tungsten-MFI zeolite membranes showed a performance of flux at 2,810 g/m^{2}h with separation factor as 32 over 80 h at 60 °C. The tungsten-MFI zeolite membranes are promising candidates for ethanol extraction with high stability. [65].

Prospects and Conclusion

Bioethanol purification can be achieved by a membrane technology known as pervaporation. The separation performance can be influenced by the process designs, membrane materials, and operating conditions. Successful pervaporation relies on fabricating membranes with high permeability, good mechanical strength, and selectivity. Review of membrane materials for ethanol and water separation have been discussed in this article.

Further enhancements can be achieved by pretreating fermentation broth with membrane separation techniques, such as micro-filtration and ultra-filtration, to remove microorganisms and by-products from the feed stream before entering the pervaporation unit. This reduces fouling on the membrane surface and allows for the recovery of microorganisms for reuse in the fermentation tank. It's important to note that membrane operation performance diminishes over time.

Membrane materials' chemical structure allows them to separate ethanol and water within a specific range of separation factors, as demonstrated in Table 1 and Table 2. A single pervaporation unit produces a solution with a particular purity. To enhance permeate purity with existing membranes, the installation of multiple pervaporation units can improve the final permeate solution.

Membrane degradation is an interesting area of research. It primarily caused by the complex compositions and by-products in the fermentation broth. Even at very low concentrations, the presence of by-products can significantly reduce membrane performance. Therefore, the exploration of higher performance and reliable membrane materials is critical for pervaporation applications in ethanol recovery [4].

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