Review Article

Review on "Membranes for Ethanol-Water Separation"

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Abstract

Bioethanol fuel produced directly from the renewable biomass is one of the truly important energy developments in Thailand. Typically, the ethanol concentration after fermentation is quite low. Normally, ethanol, as called anhydrous ethanol or absolute ethanol used for fuel energy, is required 99.5% purity or concentration. It is necessary to use energy-effective separation method for concentrating ethanol up to the fuel level. There are several techniques used to purify ethanol such as distillation, membrane technology and molecular sieve separation. Recently, the less energy-intensive technique of pervaporation is found to be a promising method for producing high-purity ethanol, but the overall economic feasibility is dependent upon the membrane. Thus, in this review, various membranes reported in literature are discussed and compared as to their advantages, disadvantages, and separation performance via the pervaporation process. It is found that different membranes provide different performances and advantages in ethanol separation. Other parameters governing the separation performance, such as temperature, ethanol concentration, membrane production method, and production cost, are also included.

***Key Words*:** Pervaporation; Membrane; Ethanol; Purification; Separation performance

Introduction

Due to the depletion of fossil fuel reserves and an increase in global demand, the development of sustainable energy alternatives for replacing fossil fuel has attracted great attention for many years, and ethanol fuel, being a good candidate, has been extensively studied. One of the reasons for ethanol's ascendancy is that it can be produced from a variety of resources, such as sugar cane, corn, grasses, etc., by fermentation. However, the current fermentation technique provides very low ethanol concentration of less than 15 wt% (Mohanty et al., 2009; Lee et al., 2013). This concentration certainly cannot be used in any engine technology; thus, in using bioethanol as the vehicle fuel, the conventional process of azeotropic distillation is used for separating the ethanol-water mixture to obtain a high purity of ethanol of at least 99.5 wt%. The azeotropic distillation, however, is an energy-intensive technique, increasing the cost of the produced fuel (Van Hoof et al., 2004; Kunnakorn et al., 2013). Other techniques, such as pressure swing absorption, liquid-liquid extraction, and crystallization, are not only costly and energy intensive, but also limited in terms of practical production (Kim et al., 2002). Membrane separation technique using pervaporation is thus an attractive process to be considered.

Pervaporation process

Pervaporation, a separation of liquid mixture using a selective membrane especially for the azeotropic and close-boiling point mixtures, is well known for less energy-intensive compared with azeotropic distillation, leading to more economically feasible processes for producing a high purity of ethanol (O'Brien et al., 2000). A liquid mixture is fed to contact with the membrane at the upstream side while the downstream side is being held under vacuum. The undesired component is able to permeate through the membrane preferentially in the form of vapor by means of the low pressure or inert gas. The desired component is concentrated by recycling the retentate to the feed reservoir, as shown in Figure 1. The

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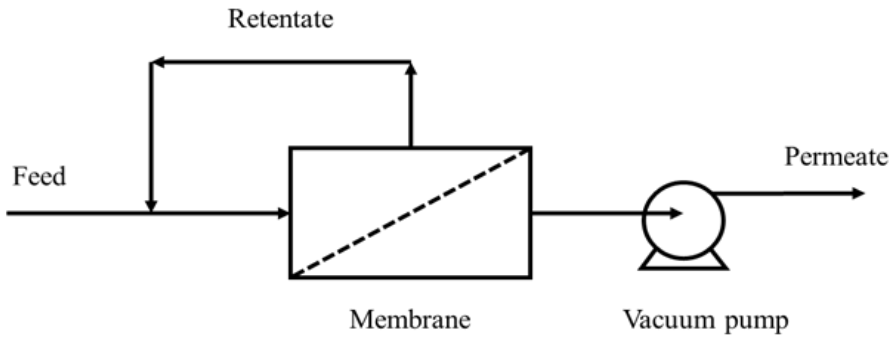

Figure 1 Schematic diagram of pervaporation process

separation performance of the membrane is determined by two major factors, permeation flux and separation factor, which relate to both the productivity and quality of the separation, as given in eq. 1 and 2, respectively.

The permeation flux (J, kg m^{-2} h^{-1}) is defined as:

$$J = \frac{W}{A.t} \quad (1)$$

where W is the weight of permeate (kg), A is the effective membrane area (m^2), and t is the pervaporation time (h).

The separation factor (α) is defined as:

$$\alpha = \frac{\left(\frac{W_{H2O}}{W_{EtOH}}\right)_{Per}}{\left(\frac{W_{H2O}}{W_{EtOH}}\right)_{REt}} \quad (2)$$

where w_{H2O} and w_{EtOH} are the weight fractions of water and ethanol from the permeate side (denoted as Per) and the retentate side (denoted as Ret), respectively.

Membrane development

Currently, the major focus of membrane development is to improve membrane performance in both high separation factor and permeation flux, thereby enhancing the economic feasibility of ethanol production (Di Luccio et al., 2002). A variety of materials have been studied in development of the membrane. In this report, the membranes for only ethanol-water mixture are reviewed and categorized into three main classes as, polymeric, inorganic, and mixed-matrix membranes. In polymeric membranes, the separating layer is made from organic polymers, while inorganic membranes are made from ceramics or zeolites. Mixed-matrix membranes are composed of both ceramic and polymer, working together for the separation (Kittur et al., 2005).

Polymeric membranes

The polymeric membrane is the most common membrane in the membrane separation process which can be fabricated by various simple techniques, such as casting, extruding, and coating. These techniques facilitate ethanol's economic feasibility in terms of membrane production costs (Chowdhury et al., 2001; Widjojo and Chung, 2009). The polymeric membrane can be used as a self-supporting membrane or supported membrane. Generally, the support for a polymeric membrane is made of porous ceramics or stronger polymer to improve the membrane strength for a better separation performance (Fu et al., 2014). The self-supporting membrane is normally cast as a thin polymer film which generally provides low mechanical properties, low separation performance, and high swelling. These drawbacks limit its application for using in the ethanol purification area (Zhao et al., 2013). Thus, many researchers have focused on improving the membrane stability as well as its separation performance by increasing crosslinking degree, blending with other polymers, and co-polymerizing with other monomers (Zhang et al., 2009). Due to the high polarity of the ethanol-water mixture, the membrane to be used in the ethanol-water separation must be hydrophilic polymers, such as poly(vinyle alcohol) (PVA), chitosan, and cellulose. However, hydrophobic membranes have also gained more attention for ethanol-water separation due to their better mechanical properties, higher chemical resistance, and higher thermal stability (Ghofar and Kokugan, 2004; Smuleac et al., 2010). Examples of hydrophobic membranes are polydimethylsiloxane (PDMS), polyimides, and a new class of phenolic resins, so-called polybenzoxazine (PBZ).

Self-supporting polymeric membranes

Praptowidodo (2005) studied the influence of two different hydrophilic groups, itaconic acid and N-3-trimethyl-ammonio-propyl-acrylamide-chloride, in PVA co-polymer membranes, and compared them with the pure PVA membrane. The pervaporation process of 90:10 ethanol:water mixture showed that the separation factor of the PVA-itaconic acid copolymer membrane was the highest, as a result of having the highest hydrophilicity, while the second copolymer containing ammonium group provided a lower separation factor, but a higher one than the pure PVA due to lower hydrophilicity. However, the permeation fluxes of both copolymer membranes were decreased due to their higher rigidity, causing brittleness. The results were in good agreement with the study of the crosslinking effect using glutaraldehyde. With an increase in crosslinking time, the separation factor increased, but the permeation flux decreased.

A PVA copolymer containing a hydrophilic group was also studied by Zhang et al. (2009). They prepared a PVA membrane grafted with quaternary ammonium group called quaternized PVA membrane using trimethyl ammonium chloride with the degree of quaternization (DQ) ranging from 2.024 to 4.035. They found that increasing the DQ value in the membrane increased the hydrophilicity and improved water selectivity, but also increased the swelling. Thus, they minimized the swelling by crosslinking the membrane using glutaraldehyde even at 85 wt% of ethanol solution, resulting in a higher selectivity. However, the permeation flux was reduced. Since a good pervaporation membrane requires high permeation flux and selectivity, these membranes must be optimized between degree of quaternization and degree of crosslinking.

Gimenes et al. (2007) prepared a blend between sericin, extracted from the silkworm cocoons, and PVA for ethanol pervaporation membrane. The dimethylolurea (DMU) was used as a crosslinking agent which was expected to crosslink only at hydroxyl groups and leave the amino groups of sericin to interact with water during the pervaporation. They found that the increase in hydrophilicity by introducing PVA into sericin caused the membrane to swell more, resulting in a higher permeation flux and lower separation factor.

Pandey et al. (2005) prepared a bacterial cellulose membrane for separation of glycerol, ethylene glycol, ethanol, formalin, and acetone from water. They claimed that bacterial cellulose was able to serve as the pervaporation membrane in an ethanol/water system, providing an excellent permeation flux of 1.43 kg m^{-2} h^{-1} at 75 °C. However, the separation factor obtained was very low, only 1.3. They explained that the membrane was not modified or crosslinked, causing the membrane to swell and resulting in such a low separation factor.

Dubey et al. (2005) worked on improving chitosan membrane by preparing chitosan/bacterial cellulose and chitosan/PVA membranes. Based on their previous work (Dubey et al., 2002), bacterial cellulose showed high mechanical strength, high chemical resistance, and good water flux. The bacterial cellulose was selected to blend with chitosan. The results showed that although the chitosan/bacterial cellulose membrane possessed a higher mechanical strength than the chitosan/PVA membrane, the membrane exhibited an identical strength to the pure chitosan membrane, meaning that adding bacterial cellulose did not improve the chitosan membrane strength. Moreover, the separation performance of the chitosan/PVA membrane revealed unsatisfactory results, showing a further reduction of permeation flux. The chitosan/bacterial cellulose also showed a moderate separation performance, but both the permeation flux and the mechanical strength were still less than those obtained from the pure bacterial cellulose membrane.

Lai et al. (2012) prepared PDMS membrane using UV/ozone treatment. Naturally, the PDMS membrane exhibits the hydrophobic property, but its surface structure could be changed by the UV/ozone treatment. Thus, the treatment was expected to change the surface hydrophobicity to a hydrophilic form, which would be more suitable for the ethanol/water pervaporation. They found that the UV/ozone treatment indeed affected the membrane surface. The working distance, relating to the UV intensity, and the pretreatment time were optimized to maximize the hydrophilicity of the membrane. However, the pervaporation results demonstrated a trade-off between the permeation flux and the separation factor after the treatment. As hydrophilicity increased, the separation factor also dramatically increased since the structure was changed to more silica-like structure, which was more restrictive to larger molecules like ethanol. However, it was also denser, reducing the total permeation flux.

Pakkethati et al. (2011) prepared PBZ membranes for ethanol/water pervaporation using a simple film-casting technique. Due to the extraordinary properties of PBZ, the PBZ was expected to exhibit higher mechanical strength and thermal stability. In their work, three different PBZs were synthesized from the bisphenol-A (BPA), formaldehyde, and three different amines, viz., hexamethylenediamine (HDA), tetraethylenepentamine

(TEPA), and tetraethylenetriamine (TETA). They found that all PBZ membranes showed a high thermal stability up to 240 °C, which is much higher than the operating temperature in the pervaporation system. The pervaporation results revealed that the fabricated PBZ membrane synthesized from HDA exhibited the highest stability with a service time longer than 120 h, a permeation flux of 1.52 kg m^{-2} h^{-1}, and separation factor of more than 10,000 at 70 °C, indicating outstanding separation performance for the ethanol/water separation with no need of additional membrane modification. They explained that the chain flexibility of the long aliphatic chain in the HDA structure played a significant role.

Le and Chung (2014) demonstrated a copolyimide membrane prepared from poly(1,5-naphthalene/3,5-benzoic acid-2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropanedimide) (6FDA-NDA/DABA) blending with its sulfonated polymer. The blend of sulfonated polymer with its pure form was expected to control the membrane performance and reduce the cost since the sulfonated polyimide provides a hydrophilicity of the membrane which increases the permeation flux, but reduces the membrane strength. According to Le and Chung, it is difficult to control the properties of the prepared membrane, resulting in poor repeatability. In their study, the preparation procedure was done by spinning process to make the hollow fiber membrane. The pervaporation result showed that the permeation flux increased when adding sulfonated polyimide, but the separation factor was lower due to the looser polymer structure, as confirmed by the increase in swelling of the polyimide blend membranes. Thus, they further studied to improve the separation factor by coating the membrane surface with PDMS layer and thermal treatment. This modification improved the membrane for the separation factor only, since the permeation flux was still reduced.

Recently, Chen et al. (2014) studied the PDMS membrane pervaporation of bioethanol produced from corn stover via fermentation process using a mixture of glucan, cellulose, and β-glucosidase enzymes. The impurities produced during the fermentation process were expected to somehow affect the pervaporation. They found that the major components were acetic acid and furan derivatives. The pervaporation with the addition of impurity was carried out individually. The effect of acetic acid was explained by the interaction between acid and PDMS, blocking the water molecules ability to diffuse through, thus reducing permeation flux. The effect of the furan derivatives was observed by using ijR value to indicate the interaction between PDMS and chemicals based on the solubility parameters. The higher ijR value obtained, the more interruption caused by the chemicals.

The separation performance data of all self-supporting membranes discussed above are summarized in Table 1. As can be seen, this membrane class is mostly produced from PVA, owing to its highly hydrophilic property. The PVA membranes provide a good separation performance with the permeation flux and the separation factor in the ranges of 0.03–0.3 kg m^{-2} h^{-1} and 10–300, respectively. However, the hydrophobic PBZ membrane has also attracted a great attention in ethanol production application because it can provide superior separation performance with the permeation flux up to 3 kg m^{-2} h^{-1} and the separation factor of over 10,000. Thus, the PBZ membrane could have a greater potential in a practical process.

Supported polymeric membranes

The limitation of self-supporting polymeric membranes, also known as unsupported membranes, in some aspects, such as poor mechanical properties, low separation performance, etc., have led to the development of the supported polymeric membranes to overcome those drawbacks (Kim et al., 2000; Wei et al., 2011). Porous ceramic materials or strong porous polymers are generally used to support the polymeric membrane. Because the molecular transport occurs in both the membrane (or separating) and the support layers, mechanical properties and separation performance are thus improved (Yoshida and Cohen, 2003).

Kim et al. (2000) prepared a thin poly(amic methyl ester) membrane on the commercial porous polysulfone support via interfacial polymerization of 2,5-bis(methoxycarbonyl terephthaloyl chloride) (BMTC) with various diamines, viz., ethylene diamine (EDA), hexamethylene diamine (HDA), and m-phenylene diamine (m-PDA), directly on the support surface. They found that poly(amic methyl ester) supported polysulfone improved the separation factor when compared to the performance of the support itself. However, the permeation flux decreased due to the increase in the transport resistance. The HDA-BMTC and EDA-BMTC membranes were found to provide superior pervaporation performance for 90:10 ethanol:water because the separating layer of these membranes was very thin while the PDA-BMTC membrane was poor in film-forming ability. Moreover, the HDA-BMTC membrane was further tested for its stability and demonstrated an excellent stability up to six days after the operation.

Yanagishita et al. (2001) studied the pervaporation performance of polyimide synthesized from pyromellitic dianhidride (PMDA) and 4,4'-oxydianiline (ODA) using poly(amic acid) salt (PAA salt), and coated on commercial

Table 1 Separation performance of self-supporting polymeric membranes

Membrane	Modification	Crosslinking agent/ condition	Feed ethanol concentration (wt%)	Temperature (°C)	Permeation flux (kg m^{-2} h^{-1})	Separation factor	Reference
PVA	-	glutaraldehyde	96	40	0.279	107	Praptowidodo, 2005
PVA	copolymerized with itaconic acid	glutaraldehyde	96	40	0.123	216	Praptowidodo, 2005
PVA	copolymerized with ammonium group	glutaraldehyde	96	40	0.119	228	Praptowidodo, 2005
PVA	quaternized with trimethyl ammonium chloride, DQ = 3.260	-	85	50	0.042	40.2	Zhang et al., 2009
PVA	quaternized with trimethyl ammonium chloride, DQ = 3.336	-	85	50	0.048	52.8	Zhang et al., 2009
PVA	quaternized with trimethyl ammonium chloride, DQ = 4.035	-	85	50	0.052	58.3	Zhang et al., 2009
PVA	quaternized with trimethyl ammonium chloride, DQ = 3.260	glutaraldehyde	85	50	0.033	58.3	Zhang et al., 2009
PVA	-	dimethylolurea	10	60	≈0.110	≈100	Gimenes et al., 2007
Sericin	-	dimethylolurea	10	60	≈0.070	≈90	Gimenes et al., 2007
Sericin	blended with PVA	dimethylolurea	10	60	≈0.095	≈125	Gimenes et al., 2007
Sericin	blended with PVA	thermally crosslinking	10	60	≈0.070	≈92	Gimenes et al., 2007
Bacterial cellulose	-	-	54	75	1.43	1.3	Pandey et al., 2005
Bacterial cellulose	treated with alkaline	-	70	70	0.112	287	Dubey et al., 2002
PVA	-	-	95	24	0.190	10.1	Dubey et al., 2005
Bacterial cellulose	-	-	95	24	0.754	1.6	Dubey et al., 2005
Chitosan	-	-	95	24	0.120	2.4	Dubey et al., 2005
Chitosan	composited with bacterial cellulose	-	95	24	0.214	9.2	Dubey et al., 2005
Chitosan	blended with with PVA (1:3)	-	95	24	0.077	19.3	Dubey et al., 2005
Chitosan	blended with with PVA (1:1)	-	95	24	0.028	22.0	Dubey et al., 2005
Chitosan	blended with with PVA (3:1)	-	95	24	0.029	2.8	Dubey et al., 2005
PDMS	-	-	90	40	0.360	11	Lai et al., 2012
PDMS	treated with UV/O_3	-	90	40	0.220	130	Lai et al., 2012
PBZ (from hda)	-	thermally crosslinking	10	70	1.52	>10,000	Pakkethati et al., 2011
6FDA-NDA/DABA	-	-	85	60	1.2	110	Le et al., 2014
6FDA-NDA/DABA	blended with 3% its sulfonated polymer	-	85	60	3.2	55	Le et al., 2014
6FDA-NDA/DABA	blended with 3% its sulfonated polymer and coated with PDMS	-	85	60	2.7	104	Le et al., 2014

asymmetric polyimide(PI-2080) support. The result showed that the performance of the supported membrane was significantly better than the self-supported one because the separating layer thickness was greatly reduced.

Li et al. (2006) worked on chitosan (CS)-PVA blends prepared on polyacrylonitrile (PAN) support for separation of ethanol, similar to the work by Jiraratananon et al. (2002), who prepared chitosan-hydroxycellulose (CS-HEC) blends on cellulose acetate (CA) support. The separation performance of the chitosan was expectedly improved by blending with a highly hydrophilic polymer, such as PVA or HEC, to increase the membrane hydrophilicity. Li et al. found that the separation factor of the CS-PVA/PAN membrane increased to maximum at 40 wt% of PVA concentration before decreased slightly, probably due to the phase inversion of the CS-PVA matrix. However, when comparing the performances between the pure CS, CS-PVA/PAN, and PVA/PAN membranes. The PVA/PAN membrane provided fair permeation flux and an excellent separation factor while the CS membrane was superior in the permeation flux, but fairly low in the separation factor. The CS-PVA/PAN membrane, however, provided a permeation flux as low as the PVA/PAN membrane, and separation factor as low as the CS membrane.

Huang et al. (2008) studied poly(thiol ester amide) prepared on the modified polyacrylonitrile (m-PAN) support. The interfacial polymerization technique was used in preparing poly(thiol ester amide) thin film by reacting cystamine (2-aminoethanethiol) with trimesoyl chloride (TMC) or succinyl chloride (SCC) on the support. They found that the poly(thiol ester amide) membrane synthesized from TMC performed better separation in terms of selectivity than the membrane synthesized from SCC because of the aromatic ring and the network structure of TMC, providing less swelling. They also measured the free volume of the membrane using Doppler-broadened linewidth and shape (S) parameters. The results confirmed the presence of the network structure in the TMC membrane and that the active layer thickness was only 100 nm, much thinner than the typical self-supported polymeric membranes.

Zhu et al. (2010) prepared PVA-chitosan membrane on a tubular asymmetric ZrO_2-Al_2O_3 support, and studied the effect of the support pore size on the performance of t-butanol/water pervaporation. It was found that the support pore size of 0.2 μm was the optimum. A too-narrow pore size of 0.05 μm provided very low permeation flux due to the high molecular transport resistance, while a too-large pore size of 0.5 μm provided very low separation factor and permeation flux because the support was not compact enough, easily causing defects. Moreover, filling of polymer into the support pores also caused a huge permeation resistance. For the separating layer, chitosan concentration was found to reduce the compactness of the PVA structure, providing more permeation flux and a slightly lower separation factor. These results were contradictory to the study of Dubey et al. (2005) who found that the structure was more compact when blending PVA with chitosan, causing further reduction of permeation flux in ethanol/water pervaporation. The membranes were further tested for various organic-water mixtures; ethanol, t-butanol, methyl acetate, and ethyl acetate, and the results showed that the pervaporation of the ethanol/water system revealed the highest activation energy.

The tubular asymmetric ZrO_2-Al_2O_3 was also studied to support PDMS membrane in the work of Wei et al. (2011). The tubular PDMS/ZrO_2-Al_2O_2 membrane was tested and compared with PDMS membrane supported by blended cellulose acetate (BCA) or PDMS/BCA membrane. The PDMS/ZrO_2-Al_2O_3 membrane was prepared by dip-coating technique while PDMS/BCA membrane was prepared by casting technique. Reduction of polymer penetration into the support and a more uniform coating when increasing molecular weight of PDMS were found to be the major reason for the increase of separation factor of the PDM/ZrO_2-Al_2O_3. The membrane thickness was found to be governed by the polymer concentration and the dipping time. The pervaporation performance result of the PDMS/ZrO_2-Al_2O_3 was not only superior, but also the long-term pervaporation results showed that the PDMS/ZrO_2-Al_2O_3 was quite stable up to 30 days with no sign of delamination while the PDMS/BCA was delaminated after 11 days of the operation.

The potential of using fully crosslinked polybenzoxazine(PBZ) membrane for ethanol/water pervaporation was studied by Chuntanalerg and coworkers (2015). Two different PBZs synthesized from bisphenol-A, formaldehyde, and tetraethylenepentamine (TEPA) and diethylenetriamine (DETA), denoted as poly(BA-TEPA) and poly(BA-DETA), respectively, were coated on tubular alumina support in order to prevent brittleness and to improve membrane strength. As both poly(BA-TEPA) and poly(BA-DETA) membrane were fully crosslinked, the swelling property was minimized, allowing them to better tolerate in a wide range of the feed ethanol concentration, from 10 to 90 wt%, with the separation

Table 2 Separation performance of supported polymeric membranes

Membrane	Support	Feed ethanol concentration (wt%)	Temperature (°C)	Permeation flux (kg m^{-2} h^{-1})	Separation factor	Reference
Polyimide (BMTC-HDA)	Asymmetric polysulfone	90	40	1.7	240	Kim et al., 2000
Polyimide (PMDA-ODA)	Asymmetric polyimide (PI-2080)	94	30	0.2	800	Yanagishita et al., 2001
HEC/chitosan	Cellulose acetate	90	60	0.424	5469	Jiraratananon et al., 2002
PVA	PAN	80	60	≈0.90	≈148	Li et al., 2006
PVA/chitosan	PAN	80	60	≈1.50	≈40	Li et al., 2006
Poly(thiol ester amide) (AETH-TMC)	Modified-PAN	90	25	1.60	1130	Huang et al., 2008
PVA/chitosan	Asymmetric ZrO_2/Al_2O_3	8	70	≈0.18	≈1300	Zhu et al., 2010
PDMS	Blend cellulose acetate	5	40	≈0.62	≈7.8	Wei et al., 2011
PDMS	Asymmetric ZrO_2/Al_2O_3	5	40	1.6	8.9	Wei et al., 2011
Fully crosslinked PBZ (poly(BA-TEPA))	α-Al_2O_3	50	70	0.0129	>10,000	Chuntanalerg et al., 2015
Fully crosslinked PBZ (poly(BA-DETA))	α-Al_2O_3	50	70	0.0120	>10,000	Chuntanalerg et al., 2015

factor values of higher than 10,000. However, the reduction of the permeation was observed at high ethanol concentration, due to the restriction of molecular transport caused by sorbed ethanol. From the study, it was found that the permeation flux of poly(BA-TEPA) membrane was reduced greater than that of poly(BA-DETA) due to the higher amount of ethanol sorption in poly(BA-TEPA).

The separation performance data of all supported polymeric membranes are summarized in Table 2. PVA was widely used as the separating layer along with chitosan. In this case, there is more than one layer involved in the separating mechanism, membrane and support layers. The major improvement of the pervaporation performance should depend on the membrane selectivity.

Inorganic membranes

Unlike the polymeric membranes, the inorganic membranes for ethanol/water separation are dominated by a single type of zeolite membrane called NaA zeolite (is referred to as zeolite A or 4A zeolite) membrane. The NaA zeolite, a sodium aluminosilicate with Linde Type A (LTA) framework, has a well-defined pore opening of about 4 Å, perfectly lying in between the molecular sizes of ethanol (kinetic diameter of 5.2 Å) and water (kinetic diameter of 2.6 Å) (Shah et al., 2000). It thus provides a molecular sieving ability in separating those two molecules, leading to a high performance membrane with an exceptional permeation flux and separation factor.

Kondo et al. (1997) prepared NaA zeolite membrane on various supports having different Al_2O_3/SiO_2 ratios. The supports were produced by mixing α-Al_2O_3, mullite, and cristobalite together. They found that the membrane selectivity increased when increasing the Al_2O3 content up to 70 % before becoming constant. However, the most cost-effective support was at 65% Al_2O_3 content, although the price of a support tube with I.D., O.D., and length of 9, 12, and 800 mm, respectively, were 1,300 JPY or about 11.18 USD.

Ikegami et al. (1999) studied the pervaporation of ethanol/water using silicalite membrane. The effects of sugars and yeast cells presented in bioethanol on

Table 3 Separation performance of inorganic membranes

Membrane	Feed ethanol concentration (wt%)	Temperature (°C)	Permeation flux (kg m^{-2} h^{-1})	Separation factor	Reference
NaA zeolite	95	95	2.35	>5,000	Kondo et al., 1997
Silicalite	4	30	0.26	23	Ikegami et al., 1999
Microporous silica	94	70	0.3-0.8	10-500	Ma et al., 2009
NaA zeolite	95	70	1.6	1760.5	Kuanchertchoo et al., 2007
NaA zeolite (with intermediate layer)	95	70	1.7	6532.7	Kuanchertchoo et al., 2007
NaA zeolite (via microwave synthesis)	87.7	70	0.5-1.0	>10,000	Kunnakorn et al., 2011a
NaA zeolite (via autoclave synthesis)	87.7	70	0.4-0.5	>10,000	Kunnakorn et al., 2011a
NaA zeolite	90	70	2.82	>10,000	Kunnakorn et al., 2011b
NaA zeolite	90	70	2.12	>10,000	Kunnakorn et al., 2013

pervaporation performance were investigated. The reduction of permeation flux was found when any of the impurities are presented in the mixture, due to the restriction of molecular diffusion by those impermeable molecules. This finding was opposite to that of Chen et al. (2014) who found that the presence of yeast cells provided a positive effect to the permeation flux for their polymeric membrane. This report was a good example of using inorganic membranes in bioethanol pervaporation in comparison with polymeric membranes.

Ma et al. (2009) synthesized microporous silica membrane for ethanol/water pervaporation. The total sample of 15 replicates was used in their pervaporation testing. They found that the separation factors and the permeation fluxes obtained were in the ranges of 10 to 500 and 0.3 to 0.8 kg m^{-2} h^{-1}, respectively. The best performance membrane, based on the optimization between the separation factor and the permeation flux, was selected for the stability test. The results showed that the membrane was stable up to 1,600 min of the operation. As time progressed, a decrease the permeation flux and an increase in the separation factor were observed. These results are similar to the results obtained from the other porous inorganic membranes, which is related to the decrease of water amount in feed.

Kuanchertchoo et al. (2006) synthesized NaA zeolite membrane on alumina support via seeding and microwave heating techniques using nano-size NaA zeolite seed synthesized from silatrane and alumatrane precursors. The advantages of using atrane precursors in the synthesis of uniformly nano-sized zeolites have been proven and reported in our previous works (Sathupunya et al., 2002; Phiriyawirut et al., 2003). The presence of NaA zeolite seed helps NaA zeolite to uniformly and continuously grow on the alumina support surface. Moreover, Kuanchertchoo et al. (2007) studied the effect of seed concentration, seeding time, reaction time and temperature on the membrane preparation. The optimization of NaA zeolite membrane was justified based on the pervaporation of ethanol/water results. They found that using 3 g of NaA zeolite seed per 1 liter of water is the optimal condition for synthesizing the membrane; amount of seed caused the membrane to become too thick, while a low amount of seed was not enough for zeolite membrane to form a defect-free continuous layer. In this study, the optimal condition for preparing NaA zeolite membrane was to use 3g/l of NaA zeolite seed with 2 min of seeding time and 15 min microwave heating time at 363 K.

Kunnakorn et al. (2011a, 2011b) compared NaA zeolite membranes synthesized from microwave and autoclave techniques. The time-dependent parameters, separation factor, and permeation flux with respect to time were studied and selected to describe the membrane stability. They found that a high purity of ethanol, at least 99.5%, for fuel specification, can be obtained from both membranes using microwave and autoclave techniques.

These membranes also provided good performance and stability in ethanol/water pervaporation for a long-term period with multiple runs, although the membrane prepared from microwave gave slightly higher permeation flux. However, judging from the preparation procedure, the autoclave technique requires significantly longer synthesis time (600 min) than the microwave heating (30 min). They also conducted a techno-economic investigation, comparing energy usage data between the conventional azeotropic distillation and the hybrid process combining distillation and membrane pervaporation systems (Kunnakorn et al., 2013). A chemical process simulation program (PRO II by Provision version 8.0) was used in the study. The simulation was based on the practical distillation process and pervaporation data obtained from the NaA zeolite membrane in their laboratory research. The results showed that the hybrid system provided the lowest energy usage in producing 99.5% ethanol. The highest amount of energy consumption was found in the azeotropic distillation column, which requires almost 20 times more energy than that utilized in the pervaporation unit.

The data of separation performance of all inorganic membranes discussed above are summarized in Table 3. As can be seen, NaA zeolite membranes exhibit the best pervaporation performance, with a permeation flux range of 1.5–2.8 kg m^{-2} h^{-1} and a separation factor of more than 10,000.

Mixed-matrix membrane

Basically, a mixed-matrix membrane (MMM), a mixture of an inorganic additive, such as zeolites, and a polymer matrix, is prepared to improve the overall separation performance, and also to overcome the trade-off barrier between permeation flux and separation factor in polymeric membranes (Robeson, 2008; Vane et al., 2008). Generally, zeolites provide exceptional separation performance, but exhibit poor ability in fabrication to achieve a homogeneous membrane.

Sun et al. (2008) prepared a MMM by incorporating H-ZSM-5, an aluminosilicate with MFI type framework with pore opening of 5.4 Å, into chitosan. H-ZSM-5 exhibits high acid strength which was expected to increase the hydrophilicity of the membrane as well as to improve the selectivity by its size-selective effect. The results showed that the H-ZSM-5/chitosan MMM improved the permeation flux. The maximum separation performance was observed when 8 wt% H-ZSM-5 was mixed with chitosan. Although addition of H-ZSM-5 into chitosan did improve the permeation flux when compared to the pure chitosan membrane, the separation factor was reduced, probably due to the larger pore size of H-ZSM-5 than the kinetic diameters of both ethanol and water molecules. They also demonstrated that an increase of the Si/Al in the H-ZSM-5 improved the permeation flux and separation factor, owing to the increase in the Si-OH-Al framework which improved the adhesion between chitosan and zeolite.

Amnuaypanich et al. (2009) incorporated zeolite 4A into natural rubber/PVA semi-interpenetrating polymer network (NR/PVA semi-IPN). The PVA was expected to improve the hydrophilicity of the hydrophobic NR matrix, while zeolite 4A, having molecular-sieving ability, was expected to improve the permeation flux and separation factor of this MMM. The increase of PVA (which in turn increases –OH group in the NR matrix caused the membrane to absorb more water due to stronger bonding to the water molecules, leading to more swelling. However, the swelling decreased with an increase in the zeolite 4A loading because the zeolite particles restricted the polymer chains movement in the matrix, reducing the total free volume of the polymer matrix. They also found that 30 wt% of zeolite 4A loading resulted in the optimal separation factor and permeation flux.

Lue et al. (2011) loaded a commercial zeolite (trade name: TZP-9023 with a Si/Al ratio of 666) into PDMS membrane. They found that the zeolite consisted of two different pore sizes of 5.93 Å (99.7%) and 29.1 Å (0.3%) with the BET surface area of 243 m^2/g. They prepared membranes using two different techniques, adding zeolite into PDMS before and after crosslinking. The pervaporation performance showed a significant improvement in post-addition membrane, while exhibiting only a slightly increase in pre-addition membrane when compared to the dense PDMS membrane. They demonstrated that the non-uniform distribution of zeolite, created by the post-addition of zeolite into the polymer matrix, enhanced the pervaporation performance while the uniform distribution of zeolite caused the chain rigidity which reduced the permeation flux.

Zhan et al. (2012) prepared PDMS/ZSM-5 (Si/Al ratio = 300) MMM loaded etched with HF acid. The etching was expected to improve the adhesion between zeolite and hydrophobic PDMS surface by reducing the hydrophilicity of the ZSM-5 at its surface. The effects of the acid concentration and zeolite loading on the membrane preparation were determined to obtain the optimal condition for a better water-ethanol separation performance. They found that the etching created the pin-holes in micrometer-scale on the zeolite surface, which later filled with PDMS, and enhanced the adhesion

Table 4 Separation performance of mixed matrix membranes

Polymer matrix	Inorganic additive	Feed ethanol concentration (wt%)	Temperature (°C)	Permeation flux (kg m^{-2} h^{-1})	Separation factor	Reference
Chitosan	-	10	80	0.054	158.02	Sun et al., 2008
Chitosan	H-ZSM-5 (8 wt%, Si/Al = 25)	10	80	≈0.119	≈178	Sun et al., 2008
Chitosan	H-ZSM-5 (8 wt%, Si/Al = 38)	10	80	≈0.119	≈165	Sun et al., 2008
Chitosan	H-ZSM-5 (8 wt%, Si/Al = 50)	10	80	0.231	152.82	Sun et al., 2008
NR/PVA	-	8.06	80	1.56	766	Amnuaypanich et al., 2009
NR/PVA	Zeolite 4A (10 wt%)	8.06	80	2.28	940	Amnuaypanich et al., 2009
NR/PVA	Zeolite 4A (20 wt%)	8.06	80	2.83	1506	Amnuaypanich et al., 2009
PDMS	-	10	25	0.002	9.21	Lue et al., 2011
PDMS	TZP-9023 (30 wt%)	10	25	0.016	12.5	Lue et al., 2011
PDMS	ZSM-5 (30 wt%, etched with HF acid)	10	50	≈0.200	≈11	Zhang et al., 2012
PDMS	ZSM-5 (30 wt%, etched with HF acid)	90	50	≈2.15	≈1.5	Zhang et al., 2012
PVA	Mesoporous silica (10 wt%, sphere shape)	90	60	0.855	42	Flynn et al., 2013
PBZ	-	10	70	0.033	>10,000	Chuntanalerg et al., 2016
PBZ	NaA zeolite (15 wt%)	10	70	1.07	>10,000	Chuntanalerg et al., 2016
PBZ	-	90	70	0.023	>10,000	Chuntanalerg et al., 2016
PBZ	NaA zeolite (15 wt%)	90	70	0.726	>100,000	Chuntanalerg et al., 2016

between PDMS and zeolite surfaces. The result was confirmed by increasing the HF acid concentration; the membrane separation factor increased while the permeation flux decreased since there was more polymer filling into the zeolite pores, decreasing the polymer chain movement, thus reducing the permeation rate. However, loading 30 wt% ZSM-5 zeolite into PDMS matrix was found to improve both permeation and separation factor. Moreover, they also suggested that this MMM was able to perform the ethanol pervaporation in all ranges of ethanol concentration of 5-90 wt%, which is suitable for bioethanol purification, but the best selectivity was achieved when the ethanol concentration was below 10 wt%.

Flynn et al. (2013) studied a MMM prepared from PVA and mesoporous silica sphere, and found that up to 10 wt% loading of mesoporous silica in PVA matrix increased the permeation flux and the selectivity before causing the drastically decreasing to below the value of those using the pure PVA membrane due to the agglomeration of the silica. The increase of permeation flux with an increase in the silica loading was explained by the increase in the membrane hydrophilicity and free volume while the increase in selectivity was claimed from the conditioning and relaxation effects.

Polybenzoxazine (PBZ) and NaA zeolite were used to prepare MMM (Chuntanalerg et al., 2016). The effects of PBZ concentration, amount of NaA zeolite loading, feed ethanol concentration, and operating temperature on the pervaporation performance were studied and discussed in this work. It was found that the incorporation of NaA zeolite into PBZ matrix, up to 15 wt%, improved both permeation flux and separation factor due to an increase in the water transportation and the molecular sieving

effect provided by NaA zeolite, respectively. However, when increasing the NaA zeolite more than 15 wt%, the defect was resulted, causing a drastically decrease of separation factor. The membrane stability evaluated in a wide range of ethanol concentration (10 to 90 wt%) was found that the degree of swelling was low, giving a high separation factor of more than 10,000 at the 10 wt% ethanol feed and went up to higher than 100,000 at the 90 wt% ethanol feed, implying that this MMM was very stable and applicable in the pervaporation of these feed mixtures.

All separation performance data described above for MMMs are summarized in Table 4. The permeation flux and the separation factor of the membranes could be simultaneously improved when adding zeolites into the polymer matrix due to its size-selective ability, which creates a promising way to achieve a higher performance.

Conclusions

Different kinds of membrane provide different characteristics. The self-supported polymeric membranes may provide an economic attraction in membrane production, but not in performance, due to their poor mechanical properties, low chemical resistance, and swelling. The supported membranes improve mechanical strength and separation performance. The inorganic membranes provide an outstanding separation performance, but are extremely difficult in processability, leading to a higher price in industrial usage. The mixed-matrix membranes thus provide an attractive alternative that are able to overcome all barriers while achieving both permeation flux and separation factor.

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