Membranes with Favorable Chemical Materials for Pervaporation Process: A Review

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Abstract

Among many purification processes, pervaporation is one of the promising technologies which is an indispensable component for chemical separations with low energy consumption, minimum contamination and ability to break up azeotropic mixtures. The key success of pervaporation process is dependent on the membrane features (chemical components and morphology). Application of membranes surveyed in three categories included organic solvent dehydration, removal of organics from solvent and separation of organic solvents. This article review discusses different types of pervaporation membranes from the perspective of membrane fabrication and materials in biofuel products.

Keywords: Pervaporation; Liquid mixture; separation technology; Diffusion

Introduction

Pervaporation (PV) process is a process for liquid mixture separation in a liquid phase. This process is able to separate different components from mixtures such as water/organic, organic/water and organic/organic mixtures. Pervaporation process works by placing a liquid mixture to be separated (feed) in contact with one side of a membrane. Across the membrane, the chemical potential gradient works as the driving force for the mass transport of the materials. Also, using vacuum pump or an inert purge (normally air or steam) on the permeate side can help to maintain of a suitable permeate vapor pressure. Usually the kept pressure is lower than the partial pressure of the feed liquid. Finally, the permeated product (permeate) can be removed from the other side with low pressure vapor (Figure 1). In terms of the application or nature of the experiment, the permeate vapor may be collected after condensation or released if desired.

Basically, hydrophilic and hydrophobic membranes apply to separate the aqueous solutions and organic solvents from water mixtures, respectively [1]. PV separation technology has superiority to other separation technologies due to the separation mechanism which is based on the difference in sorption and diffusion properties of the feed substances as well as perm-selectivity of the membrane. This mechanism is not dependent on the relative volatility of components [2,3].

Pervaporation survives the challenge of phase change by two aspects. First, pervaporation uses even with the minor components (usually less than 10 wt.%) of the liquid solutions, and second, pervaporation applies the most selective membranes. An efficient membrane need to the suitable membrane materials which can prominent efficiency of performance in the PV performance. Since the minor feed components consume the latent heat, therefore PV techniques reduce energy during the process.
membrane materials possibilities which is important in order to overcome drawbacks in current membranes.

Application of Pervaporation

Pervaporation technique as a separation process for liquid mixtures is considered to be an economic, safe and environmental friendly technology in comparison to the other conventional energy intensive technologies such as extraction or azeotropic distillation. Since PV is also well-suited for the treatment of volatile organic compounds, hence termed often as a ‘clean technology’. PV method categorize into the three different types involves dehydration of aqueous–organic solution [11], removal of volatile organic compounds from aqueous mixture [12] and separation of organic–organic solvent mixtures [13].

Currently, the fractional and azeotropic distillations have been investigated and were used to separate and concentrate alcohol/water mixture. Nowadays, these two processes are still facing suffer from high operating costs and low product yield due to their need to high energy consumption and complexity of the distillation process. The pervaporation technique shows high advantages such as low cost, easy operation and no need to purifier [14]. Potential of the industrial utility of this approach attracts for researchers to study the separation of azeotropic solution, pharmaceutical waste, isomeric and heat-sensitive liquid mixtures [15]. The separation performance of a membrane is characterized by two parameters includes flux and selectivity. Flux is the permeation rate of the feed components through unit area of membrane per unit time and measure in terms of kg m⁻² h⁻¹ or g cm⁻² s⁻¹ [16,17].

Organic solvent dehydration

To dehydrate water from the organic liquids or vapor mixtures, hydrophilic polymers as glassy polymers are suitable choices. Their glassy properties provide a good condition to make water-selective membranes which use for solvent dehydrating. Polycarbonate derivatives as samples of glassy polymers, are favourably permeable for organic compounds as compare to water [2,18,19]. The hydrophilicity property is due to the presence of the polar groups in the polymer chain that are able to interact with water molecules. Dehydration of organic solvents (e.g., alcohols, ethers, acids and ketones) is the most important applications of pervaporation membranes [4,20-23]. The importance of this process is related to the removal of water from an alcoholic compounds which are used as biofuels that extracted from a fermentation process.

Removal of organics from solutions

Separation of organic compounds from water is an important process for biofuels recovery which are produced during the fermentation process. For instance, the recovery of biofuels using PV process carry out from a solution of acetone/butanol/ethanol solution which produced by a fermenter. This process requires to a hydrophobic membrane material. Proper of the membrane materials can overcome to environmental and economic challenges. Mostly, rubbery polymer membranes are appropriate for the selective removal of organic compounds from water. However, researchers have found different kinds of membrane materials to separate various organic solvents from their aqueous solutions towards of energy efficient and economic. While among various types of membrane materials, polydimethylsiloxane (PDMS) has better results in terms of the flux and selectivity. Moreover, rubbery polymer membranes are more favorable for the selective removal of the organic compounds from water.

Separation of organic solvents

Three kinds of mixtures can be distinguished for the mixture of two organic liquids or vapors polar/apolar, polar/polar and apolar/apolar mixtures. For the removal of the polar component from polar/apolar mixture, polymers with polar groups should be chosen and for the removal of the apolar component completely apolar polymers are favorable. The polar/polar and apolar/apolar mixtures are very difficult to separate, especially when the two components have similar molecular sizes. In principle, all kinds of polymers can be used for the separation of both mixtures (polar/polar). The separation process performance on the base of differences in molecular size and shape of the mixtures. In separation of organic mixtures the temperature and pressure have more influence in the rate of transfer and selectivity of the components. However, the temperature will more effect on the organic tertiary mixtures (ABE) in comparison to the binary mixtures [24].

Recently, the ceramic and conducting polymers membranes have been studied as the selective barriers in the PV process [25-27]. Ceramic membranes provide a very high performance. They also contribute a high thermal and chemical stability to the separation process. These membranes can be used for variety applications in order to the separation organic compounds in the acidic or alkaline conditions [28].

Morphology Classification of Membrane

Membranes used in the process of pervaporation possess porous or non-porous structures. Membranes with or without pores in their structure are called porous and non-porous membranes, respectively. The schematic of various types of the membranes are shown in Figure 2. Difference of their pores size, shapes and distribution are the factors to determine pervaporation efficiency and selectivity of the membranes. In porous membranes, the permeation often carry out by size selection or exclusion. In permeating through the pores by diffusing process, such as separating water from organic solution using PV, a significant amount of water permeates across the membrane. Hence, a higher flux and lower selectivity are observed in the porous membranes. The non-porous membranes function by first partitioning the molecule and then under a concentration gradient allowing it to diffuse through the solid material. So, in the non-porous membrane the partition coefficient and diffusivity effect on the separation of components, therefore, this type of membrane is used for PV processes with high selectivity.

Composite membranes, as shown in Figure 2, commonly contain a thin dense surface coating layer above the microporous support layer and the top layer regulate the selectivity of the membrane. It is notable that the membrane materials are differ from the porous support layer [29,30]. Efficiency of mixture separation is effect by the physicochemical properties of polymeric membranes as well as operating conditions. The physicochemical properties include thickness, hydrophobicity, chemical compatibility and mechanical strength, and operation conditions include temperature and concentration gradient of the feed across the membrane. Pervaporation membranes fall into two categories, the homogeneous membranes, (Figures 2A, 2B and 2D), and the composite membrane, (Figure 2C). In the last two decades, separation performance for different binary mixtures has been studied, especially the effect of homogeneous membrane thickness [31]. Diffusion process in homogeneous membrane dominates the flux; a higher permeation...
Composite membranes, however, are not fault-free and have their own limitations. Analysis of the mass transfer resistance showed that the surface resistance of the crosslinked membrane was high for the thin membranes. Statistical analysis showed that the flux was significantly affected by the thickness of the PVA layer [37]. The selectivity was shown to be affected by the surface properties after the membrane crosslinking, especially when the membrane was thin. In the membrane morphology types, a recent development introduced a new composition membrane material which is called Mixed Matrix Membrane (MMM) [46]. MMM, as shown in Figure 2D, contains inter-penetrating polymer matrix and solid fillers, such as graphite, zeolite, silica, carbon molecular sieves, carbon fullerenes, cyclodextrin, and metal oxide [46]. The selectivity of the MMMs is around 2000 which is more than twice of neat polymeric membrane. This makes MMMs extremely suitable for breaking the azeotropes solution of water/iso-propanol [47].

Effect of Fillers on MMMs

According to the studies regarding the effect of the inorganic fillers on MMMs, some researcher reported a tradeoff between flux and separation factor, while the others reported an improvement in both flux and separation factor. Generally, the interfacial voids lead to lower selectivity but higher permeability for water. The enhancements may be attributed to the properties of fillers, their interfacial voids or the polymer chains’ rigidification by the fillers. Likewise, increase in flux can be attributed to the high hydrophilicity, high porosity and large pore size of the fillers. The sieving effect of the fillers can be caused an increase in the separation factor for water. The polymer chain-rigidification by the fillers might be a reason for an increase separation factor as the phenomenon reduces permeability. The opposite relationship among the separation factor and flux have resolved by using the inorganic fillers with right pore sizes and good polymer compatibility for a positive enhancement to separation performance [48]. A Mixed-matrix membrane might be useful for water pervaporation, as compared to the inorganic membranes.

Membranes are either hydrophilic or hydrophobic. Although most membranes are hydrophilic or water perm-selective owing to smaller molecular size of water, few membranes are hydrophobic or ethanol perm-selective. Membranes are categorized to inorganic, polymeric and composite membranes, based on the type of materials used for membrane production. The hydrophilic membranes are used for the industrial application through PV process in order to organic solvent dehydration [49,50]. Due to hydrophilic characteristics of these membranes, extraction of water with the flux and selectivity carry out depends on the active layer in the structure and its mode of crosslinks.

Hydrophilic Membranes

Based on the materials of the membranes and morphology structure of the composite, the hydrophilic membranes classify to inorganic, polymeric and hybrid composite membranes. Hydrophilic membranes are mostly used by two main membrane structures including mixed matrix and composite membranes. Many researchers have focused on the efficiency of mixed matrix and composite membranes, as well as the type of materials which improve transfer rate and selectivity parameters. The polymeric membranes are extensively studied because of their low cost and high performance as compared to the inorganic membranes. On the other hand, the inorganic membranes are excellent in the thermal stability and mechanical integrity. The hybrid membranes are a combination of the polymeric and the inorganic membranes. Their performance is affected by blend compatibility and the interactions between neighboring materials. For this reason, their structural integrity must also be analyzed other than the factors of selectivity and productivity of the composite membrane. Tailoring the substrate structure achieve a high performance composite membrane.
membranes in order to enhance the performance of the polymeric membranes.

Polymeric membrane

Pervaporation dehydration membranes divide into two categories on the base of their hydrophilicity groups. The highly hydrophilic membranes are made by polyvinyl alcohol (PVA) or chitosan. These materials are usually cross-linked to enhance their stability and reduce their swelling in pervaporation feed conditions. The commercial PVA membranes (originally made by GFT) possess high selectivity towards water with reasonably high flux [51,52]. PVA based membranes, however, are not stable with the high feed water content particularly in the high temperature operational condition [50]. Higher feed water content induces the significant swelling on the membranes and the selectivity for water decreases drastically. Hence, the membrane must be cross-linked.

In the membrane technology, there are two reasons for the polymer cross-linking, first, to make the polymer insoluble in the feed mixture and second, to reduce the degree of swelling of polymer for achieving a good selectivity. There are different methods by which cross-linking can be performed such as chemical reactions and heat treatments [53].

Commercially available polyimides such as P84®, Matrimid® and Torlon® have also been studied recently for pervaporation dehydration applications [18,54-56]. However, a long term performance of polyimides membranes has revealed a possibility of the material hydrolysis which has resulted deterioration of the separation performance over time [57]. Although polybenzimidazole (PBI) membrane possess the high thermal and chemical stability have been applied for pervaporation dehydration, its flux is relatively low due to the strong intermolecular interaction through the hydrogen bonding [58,59]. In order to modify the performance of PBI membranes for the commercial application, significant enhancement of its flux should be done. Inorganic and nano-materials were using to remove this drawback of the polymeric membranes. The materials which used in the polymeric membranes are more economic materials than the inorganic and nanomaterial membranes. Therefore, the cost of the polymeric membrane is lower than the others. Recently, researchers have decorated the polymeric membrane using oxidizing raw material like graphite to graphene oxide which reduced the cost of these membranes [60-63].

More recently, pervaporation process through the amorphous perfluoro polymers [50] have been developed to dehydrate alcohols at high temperature. The amorphous perfluoro polymers are co-polymers of tetrafluoroethylene and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole with the commercial name of HYFLO®N AD. The Hyflon membranes possess the excellent chemical resistance to dehydrate the aprotic solvents such as N,N-dimethyleacetamide [64]. The major disadvantage of these membranes is relatively lower thermal stability due to the Tg of Hyflon which is only 130°C [65]. The other researches effort to improve the separation performance.

Particularly flux with the approach of the polyelectrolytes [66,67] and thin film composite (TFC) membranes [68]. The stability of the polyelectrolytes with high amount of water is a major concern since the ionic bonding between the positive and negative ion charges of the polyelectrolytes maybe significantly weakened by the hydrogen bonding between water and the polyelectrolyte molecules. In the ultra-thin selective layer produced by the interfacial polymerization (IP), the pervaporation flux is more than 1 kg/m2 h at 25°C for dehydrating alcohols [68].

This results may be is due to the grafting or proper filler which improved the weakness of this types of polymers. The TFC membranes produced from the IP of the polyfunctional amine and acyl chloride may are not be suitable for very high temperature applications. It may find niche applications where it occur a high flux at the moderate temperature. A list of some polymeric membranes is shown in Table 1.

<table>
<thead>
<tr>
<th>commercial membrane</th>
<th>Feed compositions (wt%)</th>
<th>Feed Temperature (°C)</th>
<th>Total flux (Kg/m² h)</th>
<th>β</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P84</td>
<td>n-Butanol/water (95/5)</td>
<td>95</td>
<td>1.2</td>
<td>1000</td>
<td>[52]</td>
</tr>
<tr>
<td>Matrimid</td>
<td>IPA/water (85/15)</td>
<td>80</td>
<td>1.8</td>
<td>132</td>
<td>[17]</td>
</tr>
<tr>
<td>Torlon</td>
<td>IPA/water (85/15)</td>
<td>60</td>
<td>0.765</td>
<td>1944</td>
<td>[49]</td>
</tr>
<tr>
<td>PBI</td>
<td>Ethylene glycol/water (64/36)</td>
<td>60</td>
<td>0.732</td>
<td>303</td>
<td>[53]</td>
</tr>
<tr>
<td>Polyimide (Ube)</td>
<td>Ethanol/water (80/20)</td>
<td>100</td>
<td>0.127 (3.5 mol/m2 spa)</td>
<td>500</td>
<td>[74]</td>
</tr>
<tr>
<td>Hyflon/Cellulose ester</td>
<td>Ethanol/water (80/20)</td>
<td>75</td>
<td>1.5 (4000 GPU)</td>
<td>300</td>
<td>[47]</td>
</tr>
<tr>
<td>Polyelectrolyde</td>
<td>Ethanol/water (90/10)</td>
<td>25</td>
<td>1.75</td>
<td>600</td>
<td>[75]</td>
</tr>
<tr>
<td>Polyelectrolytes (simple GKSS)</td>
<td>Acetone/water (80/20)</td>
<td>70</td>
<td>2.15</td>
<td>60</td>
<td>[70]</td>
</tr>
<tr>
<td>PVA</td>
<td>IPA/water (90/10)</td>
<td>80</td>
<td>1.2</td>
<td>750</td>
<td>[76]</td>
</tr>
<tr>
<td>polyelectrolytes</td>
<td>Isopropanol/water (90/10)</td>
<td>50</td>
<td>1.18</td>
<td>1013</td>
<td>[69]</td>
</tr>
</tbody>
</table>

Table 1: Commercial polymeric Membrane.

The polymeric membranes show some unfavorable properties such as swelling and low performance in the permeation or separation factors, for using in the PV membranes. However, these weaknesses of the polymeric membranes can be overcome by incorporating low quantities of the specific inorganic components and nanomaterials as modifier.

Research studies were reported the highest performance of PV process when the organic compounds and nanomaterials were used.
These materials have modified some essential properties such as high permeation and low swelling in the polymeric membranes to achieve to better separation factor. Some studies have stated different advantages of the polymeric and inorganic membranes [7,69,70].

### Inorganic membranes

The membranes which are made from materials such as ceramic, carbon, silica, zeolite, various metal oxides (alumina, titania, zirconia) and metals like palladium, silver and their alloys are known as Inorganic membranes. Based on their structures, these membranes can be categorized as porous inorganic membranes and dense (non-porous) inorganic membranes [71-73]. In the first category, the microporous inorganic membranes, including both of the amorphous and crystalline membranes have two different symmetric and asymmetric structures [74].

The separation of a mixture by inorganic membrane is achieved based on the different molecular sizes of the feed mixture. Several types of the inorganic membranes have been explored for dehydration applications, including zeolite membranes [75], carbon [76,77], silica [78] and graphene [79]. NaA zeolites and silica membranes have been commercialized [7], while the other types of the inorganic membranes are still at the research stage. A first industrial plant with NaA zeolites was built in 2001 for ethanol dehydration by Mitsui Engineering and Ship building Co. The inorganic membranes have some advantages over the polymeric membrane as mentioned in Table 2.

The inorganic membranes possess high flux which are several times of the polymeric membranes. Among the inorganic membranes, the performance of NaA zeolite is still the best because of its high hydrophilicity and a pore size of 0.41 Å [7]. Using the carbon membranes prepared from the polymeric precursors have also been attempted for the pervaporation dehydration applications with some promising outcome. More recently, another type of carbon membrane, graphene oxide, has been reported for vapor permeation with ultra-high water permeability but with almost no permeation to the organic vapor [80-82].

<table>
<thead>
<tr>
<th>Inorganic Membranes</th>
<th>Polymeric Membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid structure of inorganic materials resist to swelling materials, expensive</td>
<td>Process-ability, flexibility and low cost.</td>
</tr>
<tr>
<td>Thermal and chemical stability</td>
<td>Thermal, chemical, and mechanical stability</td>
</tr>
<tr>
<td>Molecular sieve effects</td>
<td>High Selectivity</td>
</tr>
</tbody>
</table>

Table 2: Comparision of inorganic and polymeric membranes.

This is a highly interesting phenomenon and may have potential applications for the pervaporation dehydration of the organic mixtures. High costs of the inorganic membranes fabrication is a serious problem for these types of membranes. Hence, it is more efficient to use inorganic materials as a modifier not base membrane materials. Table 3 has exhibited the separation performance of the inorganic zeolitic membranes.

<table>
<thead>
<tr>
<th>Membrane Material</th>
<th>Feed &amp; Concentration</th>
<th>Operation T°C</th>
<th>Total flux (g/m2h)</th>
<th>SF</th>
<th>Membrane Structure</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite NaA/carboseptube support</td>
<td>90wt%IPA</td>
<td>70</td>
<td>300</td>
<td>2000</td>
<td>Composite</td>
<td>[80]</td>
</tr>
<tr>
<td>Zeolite NaA</td>
<td>70wt%EtOH</td>
<td>60</td>
<td>2100</td>
<td>2140</td>
<td>Composite</td>
<td>[81]</td>
</tr>
<tr>
<td>Ceramic commercial membrane</td>
<td>95wt%IPA</td>
<td>70</td>
<td>2100</td>
<td>600</td>
<td>Tubular</td>
<td>[82]</td>
</tr>
<tr>
<td>Pervap SMS® Silicamembrane</td>
<td>90wt%IPA</td>
<td>70</td>
<td>300</td>
<td>60</td>
<td>Tubular</td>
<td>[78]</td>
</tr>
</tbody>
</table>

Table 3: The seperation performance of the zeolitic membranes.

### Nanomaterials

Nanomaterials can be used as the best modifiers in membranes [63]. However they are not economical but if they use as fillers they will be economical. Using some nanomaterials such as graphene oxide (GO) can be reduced the cost of a membrane [83,84]. Many researchers are trying to improve GO properties with decorating of the flaks of GO in the PV process [63].

When nanomaterials are used as fillers they have two main advantages, firstly, low quantity of nanomaterials will give the high sufficient effects in the products, secondly, nanomaterial offer higher selectivity and mostly more stability than the inorganic fillers. Nanomaterials can easily enhance the hydrophilic polymeric or easily change the unfavorable properties of the polymeric materials [63,83,85].

Since the polymeric components are cheaper materials as the base-membrane, therefore nanomaterials are better use as modifiers. Although the organic filler improve the hydrophilicity of a membrane, nano filler get similar result with only one third of the amount of the organic filler and better performance the separation factors. Recent membrane fabrication techniques focus on GO which has considerable results on the performance in dehydration of biofuels [84,86].

Functionalizing and improving the nanomaterials can inspire a novel idea which can change the world of pervaporation by using the new materials for the membrane fabrications. Though researchers attempts to prepare the various membranes in order to dehydration process of the organic solutions and organic mixtures, they could not fabricate an economical membrane which can exhibit the equal performances in the separation and permeation simultaneously. Table 4 is shown a list of the membranes with GO.

### Comparison of PV with the Fractional Distillation

Pervaporation (PV) separation is an economical and a simple method for the separation of many organic/organic mixtures such as azeotropic solutions. It is a competitive method compared to other techniques. Unlike the fractional distillation, the separation mechanism in PV is not based on the components’ relative volatility.
In fact, it is based on the difference in the sorption and diffusion properties of the feed substances as well as the perm-selectivity of the membrane. The main advantage of PV over distillation is that PV is independent of the relative volatility of components and therefore, it is not limited by the vapor–liquid equilibrium.

Also, since the compounds which pass through the nonporous membrane are evaporated [87,88], it makes a more energy efficient method for PV as compared to the conventional distillation. In addition, pervaporation process do not show any negative influences on the micro-organisms int he fermentation broth [3,88].

Future Possibilities of PV Membrane Material

Pervaporation processes can be applied for future applications in the different fields of petrochemical industry [89,90], petroleum refinery, environment refinery, food and dairy industry, natural gas refinery and pharmaceutical aspects like process design and product control. Process design give better control of process over PV membrane to improve the quantity of the products [91-96].

Moreover, all kinds of membranes operate to make the satisfactory processes strategy for separating the polar or apolar solutions which decrease the equipment size [97-102], increase the safety, and reduce the product costs.

Pervaporation process is a suitable method for extraction of the organic-aqueous solution and organic-organic mixture due to their properties. Some of these mixtures have poor solubility in water such as toluene, benzene, ethylbenzene, and some of the other components have high solubility in water like methanol, ethanol and isopropyl alcohol [103-108]. Although fractional distillation is also a good method to extract organics such as alcohols which are highly miscible with water, the high process costs and high energy consumption are the major problems for this process. PV membrane is a preferable technique to remove these problems from industrials by breaking azetotropic barriers and/or separating water in low concentration of 10% wt.

Conclusion

Pervaporation can compete with well-established separation technologies for biofuel or alcohol separations due to distinctive advantages like economy, safety and ecofriendly nature. Overall, even though there might be some restrictions to overcome, the development of suitable membranes keeping in mind the structure property relationships of the membrane materials, membrane formation techniques and membrane modules. The full potential of pervaporation can be used in the area of alcoholic/water mixture separation. Suitable membrane materials remains a challenge for PV process from both economical and industrial application sides due to the most of the available membranes are experimented in the laboratory scale and not at industrial level. In this review paper, the different types of membranes are reviewed, as well as the challenges they face to perform better in terms of the selectivity and flux simultaneously and have long life membranes.

References


