Received: 9 October 2019

Revised: 22 March 2020

# Separation of bio-based chemicals using pervaporation

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### Abstract

The increasing demand of raw materials and the ever-present risk of fossil resource depletion are effective motivators for the development of new bio-based routes for the synthesis of chemicals. The use of non-renewable natural resources, such as fossil fuels, and the generation of greenhouse gases have led to severe environmental problems. However, one of the challenges of using renewable biomass resources to produce building block molecules is achieving an efficient and economically viable purification step. The complexity of the mixture involves generally high separation costs. Separation processes, such as distillation and liquid-liquid extraction, have been proposed to purify target bio-based compounds. However, the high energetic cost associated with such processes is pushing the current research towards the development of alternative solutions. In this context, membrane technology, such as pervaporation, is an interesting solution for minimizing the energy consumption of the process. This review highlights the main parameters and factors that impact the performance of pervaporation in the separation of complex bio-based chemical mixtures. Coupling effects, which are among the critical issues in pervaporation, are discussed in detail. Hybrid processes, in which both reaction and distillation are performed during the pervaporation process, are also addressed.

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Keywords: pervaporation; organic-organic separation; dehydration; pervaporation-distillation hybrid separation; coupling effects; biobased molecules

### INTRODUCTION

As a result of economic development and the emergence of new needs and regulations, the demand for sustainable raw materials is now a key challenge for the future. In 2015, five priorities were defined by the United Nations (U.N.) to implement 17 sustainable development goals.<sup>1</sup> Climate change is one of the main priorities, thus, research on the substitution of crude oil has been carried out since the late 90s due to the price hiking.<sup>2</sup> Recently, many efforts are focusing on the development of new technologies to produce renewable resources to replace – at least partially – petroleum-based materials.

The applications of non-renewable natural resources, such as fossil fuels, can be classified into two categories, namely energy or non-energy applications.<sup>3</sup> The typical example of energy applications is power generation from fossil fuels, which has led to a rapid growth in greenhouse gas emissions. Non-energy applications are mainly focused on the synthesis of organic chemicals and polymers. These materials can be used in a very large range of applications, including electronics, packaging, construction, sports, textiles, pharmaceuticals, plastics, food production industries, *etc.* 

In 2000, the share of non-energy applications from nonrenewable resources was 13.2% in Organisation for Economic Co-operation and Development (OECD) countries.<sup>4</sup> In 2009, 9% of all fossil fuels and 16% of oil products were used for non-energy applications, and around 330 million tons of feedstock chemicals and polymers were produced from oil-based building blocks every year.<sup>5</sup> The use of renewable resources can be the key to decreasing greenhouse gas emissions from oil-based raw materials and, in doing so, prevent further climate change.<sup>6</sup>

Even if most of the oil-based building block molecules could be produced from bio-based materials such as starch, chemical pulp, proteins, glycerol, natural fibers, or medicinal plants, most of them remain not price-competitive when compared to their petrochemical equivalents.<sup>7</sup> Biomass is a complex and heterogeneous mixture of organic and inorganic compounds that contains all kinds of solid and liquid mixtures.<sup>8</sup> Biorefineries can convert biomass into a series of products, including bio-fuel, specialty chemicals, and other valuable intermediates.<sup>9</sup> The processes in this industry can sometimes be analogous to traditional petroleum refineries,<sup>10</sup> as for example, biodiesel from different natural sources, such as oils/fats and alcohols, is produced through a

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transesterification reaction with either basic, acidic, or enzymatic catalysts.

During the process, the separation and purification of bio-based chemical mixtures are very important for producing chemicals with suitable levels of purity. Many reactions, such as transesterification reactions, produce multicomponent organic mixtures. The complexity of the mixture and its subsequent separation can be a challenging task for the process to remain economically acceptable. Physical separation, evaporation, distillation, extraction, adsorption, crystallization, and membrane separation are nowadays major technologies for separation. Membrane technology is one of the most promising, due to its low energy consumption and environmentally friendly nature. In addition, membrane separation processes can generally be carried out at low temperatures, enabling the separation of temperature sensitive chemicals.

Among the different types of membrane processes, pervaporation is a promising technology for the liquid-liquid separation of organic-water and organic-organic solvent mixtures. The selective separation of organic mixtures is a challenging issue in the chemical industry. Most industrial scale separation processes, such as conventional distillation, are energy intensive and sometimes generate a large quantity of waste due to overheating during long periods of operation.<sup>11</sup> Solvent extraction does require less energy, but the choice of the solvent has some specific requirements related to toxicity, flammability, selectivity and, of course, economy. On the other hand, pervaporation can be considered as an interesting and green solution, since no additional solvents are required. It has been applied to various separation processes, such as organic-organic separations,<sup>12</sup> waste water treatment,<sup>13</sup> dehydration during esterification reactions,<sup>14,15</sup> and dehydration of alcohol.<sup>16</sup> Pervaporation has also been combined with a reactor, leading to a reaction-separation hybrid process to improve equilibrium-limited reactions. The pervaporation membrane can selectively remove a product or a by-product from the reaction mixture, shifting the reaction to a higher production yield based on the Le Chatelier-Braum principle. In addition, pervaporation is suitable for the separation of azeotropic mixtures, because the separation mechanism is not based on the thermodynamic equilibrium but on the interaction between molecules and the membrane material. Consequently, the separation performance of pervaporation highly depends on the affinity of the molecules with the membrane materials.



Figure 1. A liquid phase zone and a vapor phase zone are divided inside the membrane

Different reviews on pervaporation separation are available, which cover several aspects, such as the use of polymeric membranes in pervaporation,<sup>17</sup> pervaporation in biorefinery applications,<sup>18</sup> separation of organic–organic mixtures, and pervaporation on fermentation processes.<sup>19</sup> In addition, some excellent books have addressed the basic theories, principles, and applications for the pervaporation membrane separation process.<sup>20–22</sup> This review aims to give a comprehensive view of the recent advances on the separation of renewable bio-based chemicals using pervaporation.

### FUNDAMENTALS OF PERVAPORATION

Pervaporation membranes are commonly non-porous dense membranes that act as a barrier in order to provide selectivity for the separation of mixed compounds.<sup>23</sup> During the process, the liquid feed mixture is transported using a pump and it contacts the active layer of the membrane. On the other side of the membrane, vacuum is applied to generate a stronger driving force. The driving force is the difference of the gradient of chemical potential on both sides of the membrane.<sup>24</sup> A phase transformation, from liquid phase to vapor phase, takes place in the membrane. The molecules diffuse through the membrane and then desorb on the permeate side. As opposed to gas permeation, the feed is liquid and is adsorbed into the polymer membrane. Thus, the membrane is partially wetted by the solution, which may produce membrane swelling.<sup>25</sup> Figure 1 shows the liquid phase zone and the vapor phase zone in the membrane during operation.

The principle of membrane transport can be modeled in two ways known as the pore-flow model<sup>26</sup> and the solution-diffusion model.<sup>27</sup> The pore-flow model contains three steps: (i) the liquid transport from the pore inlet to the liquid-vapor phase boundary, (ii) the liquid evaporation at the phase boundary, and (iii) the vapor phase transport from the phase boundary to the pore outlet. This model is usually used to describe mass transport in porous membranes, such as for ultrafiltration or microfiltration. For pervaporation, the solution-diffusion model is extensively used.<sup>28</sup> The solution-diffusion model consists of three steps, as well: (i) the sorption of the penetrant molecules in the liquid on the feed side of the surface of the membrane, (ii) the penetrant molecules' diffusion through the membrane, and (iii) the desorption of the permeate in the vapor phase on the permeate side of the surface of the membrane. Hence, the solution-diffusion model is widely applied for interpretation of transport mechanisms in the pervaporation process, as the chemical potential gradient within the membrane is expressed by the concentration gradient. A detailed derivative of equations of this model can refer to the work of Wijmans.<sup>29</sup> It is generally assumed that the thermodynamic equilibrium is reached at the interface of the membrane and the feed liquid. Thus, the transmembrane transport can be expressed as:

$$J_{i} = \frac{P_{i}^{G}}{I} (p_{i,o} - p_{i,v})$$
(2.1)

where  $J_i$  is the partial flux of component *i*,  $P_i^G$  is permeability coefficient,  $p_{i,o}$  is the partial vapor pressure of *i* in equilibrium with the feed liquid.  $p_{i,v}$  is the pressure on the permeate side, and *l* is membrane thickness. In addition, the activity can be expressed as:

$$\alpha_i = \frac{p_{i,o}}{P_i^0} \tag{2.2}$$

where  $P_i^0$  is the saturation pressure of component *i*.

For non-ideal mixtures, the activity of each component is written as:

$$\alpha_i = x_i \times \gamma_i \tag{2.3}$$

where  $x_i$  is the molar fraction and  $\gamma_i$  is the activity coefficient of component *i*.

The driving force is the difference of partial pressure across the membrane and it can be determined by:

$$p_{i,o} - p_{i,v} = x_i \times \gamma_i \times P_i^0 - y_i \times P_p \tag{2.4}$$

The saturated vapor pressures ( $P_i^0$ ) are typically determined from the Antoine equation<sup>30</sup>

$$P_i^0 = 10^{A - \frac{B}{C + T}}$$
(2.5)

where *A*, *B*, and *C* are constant and *T* is temperature. The static method is employed to estimate these three coefficients. This technique is based on the measurement of the pressure over a degassed pure sample introduced in a thermo-regulated cell under ultra-high vacuum at various temperatures.<sup>30</sup> The Antoine relation gives a very good approximation of the vapor pressure of a pure compound within the temperature range of the experimental data.

The vapor pressure of the components in the feed is an important factor in determining the performance of permeation, as well as the pressure applied in the permeate side. The effect of pressure on transmembrane flux has been studied by Greenlaw *et al.*, who observed that, as expected, a higher transmembrane flux can be obtained when the pressure in the permeate side is decreased.<sup>31</sup>

The experimental performance of pervaporation is typically evaluated by studying the transmembrane flux, separation factor, permeance (or permeability), and selectivity.

The transmembrane flux J (kg/m<sup>2</sup> h) is usually determined by the weight of the collected permeate over a certain period of time, divided by the effective membrane area:

$$J = \frac{w}{\Delta t \times A} \tag{2.6}$$

where A is the active surface area of the membrane (m<sup>2</sup>),  $\Delta t$  is the collecting time (h), and w is the weight of permeate (kg).

The concentration in the feed and permeate  $(y_i)$  can be determined by gas chromatography, for example. Therefore, the experimental partial flux for each component  $(J_i)$  can be determined by the following equation:

$$J_i = J \times y_i \tag{2.7}$$

The permeance  $\binom{P_i}{T}$  or permeability  $(P_i)$  of each component is calculated by dividing the partial molar flux by the driving force, according to Eqn. 2.1. Therefore, the impact of the driving force is eliminated. It can be expressed according to Eq. (2.8).

$$\frac{P_i}{l} = \frac{J_i}{\left(x_i \times \gamma_i \times P_i^0 - y_i \times P_p\right)}$$
(2.8)

The total pressure of the permeate side  $P_p$  is measured during the experiment. The permeance is usually expressed in GPU (1 GPU =  $1 \times 10^{-6}$  cm<sup>3</sup> (STP)/(cm<sup>2</sup>s cmHg) and 1 m<sup>3</sup> m/ m<sup>2</sup>s kPa =  $1.33 \times 10^{8}$  GPU).

The separation factor is a parameter determining the separation performance. It is defined as the ratio between the molar concentration of each component (*i*, *j*) in the permeate ( $y_i$ ,  $y_j$ ) and feed ( $x_i$ ,  $x_j$ ) solutions:

$$\beta_{i/j} = \frac{y_i/y_j}{x_i/x_j} \tag{2.9}$$

As the transmembrane flux and separation factor are influenced by the operation conditions, such as feed concentration, permeate pressure, and feed temperature, the transmembrane flux and separation factor cannot reflect the affinity between molecules and membrane materials. Therefore, permeability (or permeance) and selectivity are introduced in order to eliminate the impact of the driving forces.<sup>32</sup> As a result, these parameters are related to the intrinsic separation properties of the membrane.

The selectivity of the membrane is given by the ratio of permeance or permeability:

$$\alpha_{i/j} = \frac{P_i/I}{P_j/I} = \frac{P_i}{P_j}$$
(2.10)

If the value of  $\alpha_{i/j}$  is larger than 1, it indicates that the membrane is more preferential to permeating component *i* than component *j*.

### FACTORS AFFECTING PERVAPORATION MEMBRANE PERFORMANCE

# Influence of feed composition on the membrane performance

Influence of feed composition on polymeric membrane swelling and plasticization

Polymeric membrane swelling is a phenomenon resulting from the diffusion of solvent molecules into the polymer chains that leads to the expansion of the polymer network.<sup>33</sup> As polymerpolymer interactions remain stronger than polymer-solvent interactions, the dissolution of polymeric membrane does not occur. In the separation of bio-based chemicals via pervaporation, when a liquid mixture contacts the membrane, the components usually cause swelling resulting in an increase of the free volume within the polymeric matrix. The membrane swelling phenomenon has an important impact on the membrane performance, affecting the permeability of the different components and, therefore, the selectivity of the separation. For example, water can cause membrane swelling during dehydrating processes. In the study of hybrid membranes of zeolitic imidazolate framework-L (ZIF-L) and zeolitic imidazolate framework-8 (ZIF-8) for dehydrating bioethanol,<sup>34</sup> the membrane experienced excessive swelling at high water concentrations leading to an increase of both water and ethanol fluxes due to the rise of water concentration in the mixture. It was observed that ethanol flux increased dramatically for high concentrations of water in the mixture. Ethanol is sensitive to the expansion of polymer chain spacing because it has a larger

kinetic diameter.<sup>35</sup> As a result, the separation factor decreased with the increase of water concentration. In addition, the permeance of water and ethanol also increases with the increase of water concentration, leading to a decrease in the selectivity.

A plasticization effect may happen due to the increase of the membrane swelling degree. The presence of specific chemicals inside the membrane can change the mechanical properties of a given polymer and lead to a more flexible material, therefore increasing the diffusivity of the permeant.<sup>36,37</sup> The concentration of the individual chemicals in the mixture can also influence the plasticization effect due to the potential interaction between specific chemicals and the membrane. MTBE bio-derived version of methyl tert-butyl ether (MTBE), which was produced from isobutene and biomethanol.<sup>38</sup> However, a methanol and MTBE mixture can form azeotropes at a composition of 14.3 wt% methanol.<sup>39</sup> Hence, the distillation process is expensive and has a high energy consumption. In the work by Cao et al.,<sup>40</sup> the separation of a methanol/methyl tert-butyl ether (MTBE) mixture with a cellulose triacetate membrane was studied in order to break the azeotrope for the production of bio-MTBE. During the pervaporation of the methanol/MTBE mixture (concentration of methanol in the feed of 13.04, 19.41, and 37.52 wt%), the plasticization effect was enhanced when the methanol concentration was increased in the mixture, resulting in an enhancement of the permeation of MTBE due to a larger free volume. A significant phase transition of the polymer from glassy to rubbery takes place on the feed side. As a result, the polymer plasticization effect becomes significant due to excessive membrane swelling, which increases the polymer chain spacing dramatically. This effect facilitates the permeation of MTBE through the membrane.<sup>41</sup> Plasticization effect has, then, a strong negative impact on the performance of the pervaporation membrane in terms of both selectivity and separation factor.

As excessive membrane swelling leads to lower membrane separation performance, some research was carried out to reduce it. The swelling effect can be counterbalanced by introducing another polymer. Ethyl tert-butyl ether (ETBE) is also known to be a powerful octane enhancer like MTBE. Compared to MTBE, ETBE has less environmental impact because MTBE has been found to be responsible for groundwater contamination.<sup>42</sup> It is expected that ETBE demand will increase due to the concern of MTBE toxicity. However, it is a challenge to produce low cost ETBE in petrochemistry.<sup>43</sup> Traditionally, partially renewable bio-ETBE is obtained from the reaction of bio-ethanol (in excess) with isobutylene obtained from fossils. Tretbar et al. performed the etherification of fermentative-produced isobutylene and bio-ethanol (in excess) to produce fully renewable bio-ETBE.<sup>44</sup> However, the obtained ethanol/ether mixture is difficult to separate by conventional separation processes, such as distillation, due to the existence of azeotropes. In the separation of the mixture of ethanol/ ethyl tert-butyl ether (ETBE) with polypyrrolidinone membrane blended with N-[3-(trimethylamoniopropyl)] methacrylamidemethylsulfate (TMA),45 pyrrolidinone was found to strongly increase the membrane affinity for ethanol. However, the membrane can swell severely in the presence of ethanol. As a result, a coupling transport phenomenon was observed: the higher the ethanol concentration in the feed, the higher the ETBE flux through the copolymer membrane, leading to a drop in selectivity. When TMA polymer was introduced in the copolymer membrane, crosslinking of TMA with the matrix prevented the membrane swelling, which comes from ammonium sulfate residues (strong polar feature). By doing so, the swelling effect, which results from pyrrolidinone swollen by excess ethanol, can be reduced. Therefore, a higher amount of TMA in the copolymer membrane leads to a lower transmembrane flux but does improve the membrane selectivity.

#### Hansen solubility parameters of the feed mixture

Hansen solubility parameters are usually used for selecting the proper solvent to dissolve polymer materials. In pervaporation, Hansen solubility parameters are used for the study of the interaction and affinity between molecules and the membrane material, and have been widely applied in the selection of materials for membranes. Hansen<sup>46</sup> proposed an approach to predict the solubility of components into a polymer based on three main parameters: a dispersion component, a polar component, and a hydrogen bonding component. A point can be determined by these three parameters in a three-dimensional space, forming a sphere. The center of the sphere is determined by the solubility parameters of the polymer and the radius of the sphere is called the interaction radius, which is measured experimentally and reported in the literature.<sup>47</sup> A component is more likely to be sorbed by the membrane if the solubility parameters of the component are located within this three-dimensional sphere. The distance of the component to the center of the polymer solubility sphere is calculated by the following equation<sup>4</sup>

$$R_{a} = \left[4\left(\delta_{Ds} - \delta_{Dp}\right)^{2} + \left(\delta_{Ps} - \delta_{Pp}\right)^{2} + \left(\delta_{Hs} - \delta_{Hp}\right)^{2}\right]^{1/2}$$
(3.1)

where  $R_a$  is the distance between the component and the center of polymer solubility sphere (MPa<sup>1/2</sup>), and  $\delta$  refers to the Hansen solubility parameters. The first subscripts, *D*, *P*, and *H*, refer to the Hansen component: dispersion component, polar component, and hydrogen bonding component, respectively; the second subscripts, *s* and *p*, refer to the component and polymer, respectively. If the distance of the component to the center of the polymer solubility sphere  $R_a$  is smaller than the interaction radius of polymer  $R_0$ , then the component could be sorbed by this polymer.

The Hansen solubility parameters of a mixture are estimated as expressed in Eqn. (3.2), reported by Barton *et al.*<sup>48</sup>

$$\bar{\delta_k} = \sum_i \phi_i \delta_{ki} \tag{3.2}$$

where the subscript k indicates the D, P, and H Hansen components (dispersion component, polar component, and hydrogen bonding component, respectively).  $\phi_i$  is the volume fraction of different pure components in the mixture.

As solubility parameters depend on the composition of the mixture, the position of the solubility parameters of a mixture mapping on the three-dimensional space shifts from their pure solution. Therefore, when shifting towards the center of the polymer sphere, the mixture is more likely to be sorbed by the membrane. In the case of the pervaporation separation of an organic liquid-water mixture by a copolymer membrane (polydimethylsiloxane and ladder-like phenylsilsesquioxiane),<sup>49</sup> it was found that the transmembrane flux and separation factor follow the trend methanol<ethanol<2-propanol<acetone<THF. This sequence corresponds to the decrease of solubility parameters of these organic compounds, regardless of their molecular size. Therefore, in this case, the permeation behavior is determined by the solubility parameters of the organic compounds. In other words,

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according to the solution-diffusion model, sorption is more dominant than diffusion in the permeation of these organic compounds.

The difference of solubility parameters between pure components and mixtures was studied by Li et al.<sup>50</sup> Two transesterification mixtures (methyl acetate, butanol, butyl acetate, and methanol; and methyl acetate, ethanol, ethyl acetate, and methanol) were investigated. The product butyl acetate is an important and useful solvent for various applications, for example, paint and coating manufacture and the lacquer industry. On the other hand, the product methyl acetate is one of the compounds in the production of biodiesel. These esters, methyl acetate, butyl acetate, and ethyl acetate can be derived from bio-alcohols. In addition, these transesterification reactions contain a quaternary organic mixture with azeotropes (methyl acetate/methanol, ethyl acetate/ethanol, and butyl acetate/butanol). It was found that pure esters did not permeate through the commercial membranes Pervap 1255-50 and 4155-80 (Sulzer), but they did when the feed consisted of a mixture of esters and alcohols. The presence of alcohols enhanced the permeance of esters through the membranes. The 3D representation of the Hansen solubility sphere and its projection into hydrogen-polar plane and hydrogendispersion plane at 30 °C are reported in Fig. 2. As commercial membranes are made of poly vinyl alcohol (PVA) material, all pure alcohols are located inside of the PVA polymer solubility sphere. Yet, all esters are located outside of the PVA polymer solubility sphere (Fig. 2). This indicates that the PVA membrane favors the permeation of alcohols rather than the permeation of esters. As for solutions of alcohol and esters, both mixtures are located inside the PVA solubility sphere (shown in Fig. 2). As a result, all components in the mixture can be sorbed by the PVA membrane and then diffuse through it.

The solubility parameter indicates the affinity between the organic compound and the polymer, and it is also related to the membrane swelling.<sup>51</sup> In the work by Yamaguchi et al.,<sup>52</sup> the solubility of 54 kinds of organic compounds and water through a poly methyl acrylate (PMA) membrane prepared by plasma graft polymerization was studied, classifying each mixture as soluble or insoluble for the membrane. In the separation of benzene-cyclohexane mixtures, according to the solubility parameter prediction, the PMA membrane showed a high affinity to benzene for a large range of concentrations. However, the transmembrane flux increased and the separation factor decreased when the benzene concentration was increased in the feed, since the solubility parameter of the mixture was getting closer to the center of PMA three-dimensional sphere. It indicates that the mixture - and especially benzene has more affinity with the polymer membrane. As a result, the degree of membrane swelling increased due to the higher benzene concentration and a plasticization of the polymeric membrane can occur. Consequently, the selectivity of the pervaporation membrane was reduced due to this plasticization effect.

In summary, solubility parameters are a useful tool not only to screen and select membrane materials for a targeted separation of bio-chemicals, but also to predict potential membrane swelling and the possible affinity between membrane material and components.

### Effect of the pH of the feed on membrane performance

Organic acids, such as formic acid, acetic acid, lactic acid, propionic acid, or butanoic acid, are important bio-based building blocks. A large number of catalytic systems have been developed to convert biomass (including cellulose, lignin, etc.) into organic acids, which can be used directly or be modified for further applications.<sup>53,54</sup> The pH value is an important parameter, for example, organic acids as charged compounds will not be able to diffuse through the pervaporation membrane.<sup>30,55</sup> For Brønsted acid/ base, the charge of the different species is directly related to the pH of the solution. It is therefore mandatory to have a clear view of the speciation of the components at different pH levels, prior to designing a pervaporation process.

In the work of Overington et al.,<sup>56</sup> pervaporation was used to separate organic acids (acetic acid, butanoic acid, hexanoic acid, and octanoic acid), ketones (2-heptanone and 2-nonanone), and esters (ethyl butanoate, ethyl hexanoate and ethyl octanoate) out of mixtures. At a low pH (2.5-3.5), more than 94% of organic acids were in the non-dissociated form in the feed mixture, and the enrichment factor (the ratio of a component concentration in the permeate to its concentration in the feed) was the highest for these organic acids. When the pH level increased from 2.5 to 4.8 and further increased up to pH 7, more compounds were in their carboxylate forms and a lower enrichment factor was observed. At pH 7, the enrichment factor of these organic acids was decreased to 84%. As fewer organic acids can be adsorbed by the hydrophobic polydimethylsiloxane membrane at those pH values, the competition between permeants to access the sites in the membrane becomes less stringent. Esters and ketones have more opportunities to occupy the sites and permeate through the membrane at these pH values. Hence, organic acids were concentrated more effectively when the pH level remained below 3.5.

In other cases, a low pH is not favorable for the pervaporation. Silicalite (one of the polyforms of silicon dioxide, SiO<sub>2</sub>) membrane is an ethanol permselective membrane. This membrane can be directly used to produce highly concentrated bioethanol via fermentation-pervaporation process. However, the pervaporation performance could be deteriorated due to the presence of succinic acid, which can be adsorbed by the silicalite membrane. Ikegami *et al.* studied the pervaporation performance of a ternary mixture of ethanol/water/succinic acid.<sup>57</sup> The ethanol permeation decreased dramatically at pH levels below 5 because the concentration of the acid form of succinic acid increased. As a result, more succinic acid can be adsorbed by silicalite membrane, resulting in a major decrease of ethanol permeation.

#### Effect of temperature on membrane performance

Temperature is one of the most important factors affecting membrane performance. The interpretation of its effect can be rationalized by analyzing the activation energy. The transport rate of the permeant passing through the membrane depends on sorption and diffusion. Therefore, the permeability can be defined as the product of the diffusion coefficient and the sorption coefficient:<sup>58,59</sup>

$$P_i = D_i \times S_i \tag{3.3}$$

where  $D_i$  and  $S_i$  are the diffusion coefficient and solubility coefficient of component *i* in the membrane, respectively. Both coefficients are temperature dependent. This dependency is typically described by the following Arrhenius-type equation:<sup>58,59</sup>

$$S_i = S_{i,0} \exp\left(\frac{-\Delta H_{i,S}}{RT}\right)$$
(3.4)

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**Figure 2.** Hansen solubility sphere for PVA with pure components and mixtures of alcohols and esters at 30 °C (a) 3D representation; (b) Projection into the hydrogen-polar plane; and (c) Projection into the hydrogen-dispersion plane. The composition of mixture 1 (molar fraction) is 0.2 methyl acetate, 0.15 butyl acetate, 0.35 methanol, 0.3 n-butanol; the composition of mixture 2 (molar fraction) is 0.2 methyl acetate, 0.35 methanol, 0.3 methanol, 0.3 ethanol. Reprinted with permission from Li et al<sup>50</sup>

$$D_i = D_{i,0} \exp\left(\frac{-E_{i,D}}{RT}\right)$$
(3.5)

where  $S_{i,0}$  and  $D_{i,0}$  are temperature-dependent constants.  $\Delta H_{i,5}$  is the heat of solution or enthalpy of dissolution.  $E_{i,D}$  is activation energy for diffusion. Using equation  $P_i = D_i \times S_i$ ,  $P_i$  can be defined as described in Eq. (3.6).

$$P_i = D_{i,0} S_{i,0} \exp\left(-\frac{\Delta H_{i,S} + E_{i,D}}{RT}\right)$$
(3.6)

Thus, the activation energy of permeation is expressed by the following equation:  $^{60}$ 

$$E_{i,P} = E_{i,D} + \Delta H_{i,S} \tag{3.7}$$

An increase of temperature improves diffusion, so the activation energy of diffusion  $E_{i, D}$  is usually positive. It is the energy to produce free volume between the polymer chains that allows the permeant molecule to diffuse through and jump from one created free volume to another.<sup>61</sup> The heat of solution is the heat

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generated or absorbed during the sorption process, which also depends on the sorption mechanisms dominating the process.<sup>62</sup> If the sorption follows Henry's law, the sorption process will be endothermic, as a site has to be formed prior to the molecule sorption. In the case of Langmuir sorption, the molecule is sorbed by a site that already exists in the polymer matrix, presenting an exothermic sorption. A low activation energy indicates that the molecules must overcome a low energy barrier for permeation through the membrane.

By combining Eqns (3.6) and (3.7), the temperature effect on the permeance can be evaluated: $^{63}$ 

$$\frac{P_i}{I} = \frac{P_{i,\infty}}{I} \times \exp\left(-\frac{1000 \times E_{i,P}}{RT}\right)$$
(3.8)

where  $P_i/I$  is the permeance of the component *i*,  $P_{i, \infty}/I$  is the preexponential factor of permeance with  $P_{i, \infty} = D_{i, 0}S_{i, 0}$ , indicating the permeance at infinite temperature, and  $E_{i, P}$  is the activation energy.

The dehydration of butyl acetate is a good example of the impact of activation energy on permeance due to the temperature effect.<sup>64</sup> The blended membrane made of polyvinyl alcohol (PVA) and chitosan (CS) gave a better separation performance at high temperatures (70 °C). The activation energy of water was 23.77, and -56.44 KJ/mol for butyl acetate. The activation energy illustrates the sensitivity of a molecule's permeation to temperature. As the activation energy of water is positive, its permeation behavior is dominated by diffusion. However, for butyl acetate, the activation energy is negative, which means that the permeation behavior is controlled by sorption: a higher temperature is not favorable for the molecule permeation. As a result, the permanence of water increased linearly and the permanence of butyl acetate decreased with the rise in temperature. Due to this contradictory permeation behavior between water and butyl acetate, the separation performance is significantly improved at higher temperatures. Another typical example was described by Adymkanov et al.<sup>65</sup> The temperature effect on permeation was studied for water, ethanol, and butanol from 30 to 50 °C. It shows that the activation energy is an important factor on selectivity. It was found that water had a higher activation energy than alcohols in the PIM-1 (polymers with the inner microporosity) membrane. Higher temperatures can promote the permeation of water, hence the selectivity (towards alcohols) of this hydrophobic membrane tends to decrease with increasing temperatures.

Apart from the temperature effect, the composition of the mixture can also have an impact on the activation energy. In the purification of ethanol from methanol using polybenzoxazinoneimide (PBOI) membrane,<sup>66</sup> the activation energy for the permeation of methanol is generally lower than that of of ethanol (Fig. 3). Methanol must overcome a lower energy barrier than ethanol for permeation through the membrane. Therefore, the membrane shows a better permeation to methanol. On the other hand, when the concentration of methanol increases in the feed, its activation energy of the permeation decreases. Figure 3 shows that the activation energy of the permeation of methanol was the highest for 20 wt% of methanol in the feed and the lowest for 5 wt% at the same temperature.

As indicated in section 3, the transmembrane flux and separation factor depend on the driving force (see Eqn. (2.4)). On the other hand, from the Antoine equation (Eqn. (2.5)), it can be observed that an increase in temperature leads to an increase of



**Figure 3.** The logarithmic dependence of individual fluxes on temperature in pervaporation of methanol/ethanol mixtures of different composition. Reprinted with permission from Pulyalina et al.<sup>66</sup>

the saturated vapor pressure. As a result, the driving force is improved by increasing the temperature. Hence, an increase of temperature can have a positive impact on the transmembrane flux. On the permeate side, the partial pressure is extremely low, thus, the term  $y_i \times P_p$  in Eqn. (2.4) is normally negligible. For example, for the dehydration of a medium during an esterification reaction between lactic acid and ethanol via a chitosan-TEOS (tetraethoxysilane) membrane,<sup>67</sup> the vapor pressure of all penetrants increased with temperature. As a result, the partial pressure gradient across the membrane increased, enhancing the driving force for each penetrant. In the meanwhile, the partial flux of ethanol increased more steadily than that of water due to its higher volatility.

In some cases, temperature can have a complete opposite influence on transmembrane flux and permeance.<sup>68</sup> Increasing temperature leads to an increase in transmembrane flux, but a decrease of permeance. Transmembrane flux and separation factor depend on the operation conditions related to the driving force. However, permeance and selectivity reveal the real interaction between the molecules and membrane materials. A high permeance indicates that the affinity between certain molecules and the membrane material is high and, therefore, the membrane is keen on letting this molecule permeate. Therefore, the evaluation of the thermodynamic properties of the target mixture and the intrinsic properties of the membrane for separating the mixture are essential when aiming at developing a new pervaporation process for the separation of bio-molecules. Luis et al.63 studied the quaternary mixture composed of methanol, methyl acetate, butanol, and butyl acetate as a case study. A procedure is proposed to evaluate the separation potential of pervaporation membranes and it consists of three steps. First, the driving force of each compound has to be evaluated, and the compounds with the largest driving force can be determined as target compounds for permeation. Secondly, the permeances and selectivities of membranes must be assessed experimentally; the optimal situation is when the membrane can enhance the permeation of the compounds with the highest driving force observed in step 1. Third, a McCabe-Thiele separation diagram is set up for comparing the separation properties of pervaporation membranes and the performance with distillation. With this procedure, it can be determined if a pervaporation process is able to achieve optimal performance under certain conditions.

### Effect of membrane thickness on membrane performance

Membrane thickness is another important factor in optimizing the performance of pervaporation membrane separation of biomolecule mixtures. A general rule is: the thicker the membrane, the lower the flux and, hence, the higher the selectivity.

A low thickness usually reduces selectivity. Such an effect has, for example, been observed by Brun et al. on 1,3-butadiene.<sup>69</sup> Traditionally, 1,3-butadiene is a by-product of the stream cracking of naphtha of petroleum used to produce ethylene. Due to the sustainability concerns of consumption of fossil stock, a renewable route to produce 1,3-butadiene from bio-butanol has been proposed.<sup>70</sup> The purification process includes the separation of 1,3-butadiene and isobutene, an intermediate product which is generated during the butanol dehydration step. In the case of the pervaporation separation of a mixture of 1,3-butadiene and isobutene (60/40 volume fraction), it was observed that the transmembrane flux was inversely proportional to the nitrile rubber membrane thickness (12-500 µm), up to 100 µm.<sup>69</sup> Above this value, the selectivity was independent from the membrane thickness. In this case, the membrane material is an elastomer and made up of very thin grains. Therefore, highly tortuous micropores exist inside the membrane material. When the size of the membrane thickness is comparable to the size of thin grains, a micro-pore diffusion can occur.

The defects inside a membrane also have a significant influence on the performance of a thin membrane. Acetic acid can be produced via microorganism fermentation, a purification process being introduced to remove water as a by-product.<sup>71</sup> While using polysulfone (PSF), Polyvinyl chloride (PVC), and polyacrylonitrile (PAN) membranes to dehydrate acetic acid, a linear relationship was found between the total flux and the membrane thickness.<sup>72</sup> Regarding the selectivity, it was dependent on the membrane thickness for values below 15 µm, where it decreased with the membrane thickness. This phenomenon is explained by the formation of defects during pervaporation, regardless of polymer morphology or transport coupling. When a critical strain of polymeric material is reached, crazes and cracks can be formed. In a chemically active environment, the formation of crazes can be intensified when the polymeric materials undergo plasticization leading to a lower surface energy of polymeric materials, which is favorable for the formation of crazes. The transportation through these solvent-induced craze defects could be described by Knudsen flow.

Similar observations can be found in chitosan membranes for the separation of water-ethanol mixtures.<sup>73</sup> In this case, the transmembrane flux does not always follow Fick's law and selectivity is a function of membrane thickness for values below 30 µm. On the other hand, a higher and constant selectivity can be observed when the membrane thickness is higher than 50 µm. The selectivity begins to decrease when the membrane thickness decreases below this point. Hence, a minimum membrane thickness is essential to determine its intrinsic selectivity. Meanwhile, the partial flux of each component shows a reversely proportional relationship to the membrane thickness when membrane thickness is high, and this phenomenon is independent of feed concentration. A non-Fickian behavior of partial flux is observed at a low membrane thickness; a lower membrane thickness presents a higher partial flux. This phenomenon is interpreted by the growth of crazes in the direction of diffusion when the liquid is enriching at the tip of crazes. Koops *et al.* suggested that a minimum membrane thickness has to be determined to stop the growth of crazes, because part of the flux was caused by them.<sup>72</sup> The crazes can break through a swollen layer of the membrane due to the lack of mechanical stability. Their growth is easier in thinner membranes, and part of the flux caused by them contributes to the overall membrane flux.<sup>74</sup>

Besides, Kanti et al. tested different thicknesses, ranging from 25 to 190 µm, for blended membranes of chitosan and sodium alginate. These membranes were studied for the dehydration of an ethanol-water mixture (95.4-4.6 wt%).<sup>75</sup> For this system, the flux gradually decreased with an increase of the membrane thickness in the same experimental conditions, because the diffusion rate decreases when the membrane thickness increases. On the other hand, the selectivity increased dramatically (from 436.3 to 2118.5) with increasing membrane thickness. The variation of selectivity regarding the membrane thickness was related to membrane swelling and plasticization. The active layer was seriously swollen and plasticized for thinner membranes, allowing all the permeating components in the feed solution to diffuse through the membrane layer unrestricted. Thicker membranes, however, can be only partially swollen and plasticized. Hence, the thickness of a non-swollen layer increased with the entire membrane thickness of the active layer, leading to an increase of mass transfer resistance inside the membrane. The non-swollen layer becomes a restrictive barrier and only allows certain penetrants to diffuse through, which results in decreasing flux and enhancing selectivity. Similar phenomena were also observed in the separation of a water acetamide mixtures by chitosan membrane.<sup>76</sup>

On the other hand, a thicker membrane increases the mass transfer resistance resulting in a decrease of flux. Villaluenga et al. studied the mass transfer behavior in terms of a resistancein-series model with cellulose acetate membrane and poly(2,-6-dimethyl-1,4-phenylene oxide) membrane for the separation of a methanol/MTBE mixture.<sup>77</sup> The liquid membrane boundary layer resistance was larger than the membrane resistance when a thinner membrane was used. With the increase of membrane thickness, the membrane resistance became a more important factor on mass transfer in the membrane, and the liquid membrane boundary layer resistance was lower than the membrane resistance. The critical membrane thickness on which mass transport resistance is dominated between the liquid membrane layer resistance and membrane resistance was determined by Villaluenga et al.<sup>77</sup> In this case, for the cellulose acetate membrane, this thickness value is between 23 and 33 um and for the poly(2,-6-dimethyl-1,4-phenylene oxide) membrane, it is around 38 μm.

As discussed above, an optimal membrane thickness is important for the performance of pervaporation separation. A minimum membrane thickness must be determined to have an intrinsic selectivity. In the meanwhile, a thicker membrane active layer can decrease the transmembrane flux.

### **COUPLING EFFECTS IN PERVAPORATION**

Coupling effects are important phenomena observed frequently in pervaporation processes. The mass transport in the membrane is a complicated process because of the existing interactions between the permeants and between the permeants and the membrane itself. Coupling effects are difficult to measure quantitatively, but it is possible to obtain indirect information from the partial flux of each component or via sorption and desorption experiments.<sup>78</sup> In most of pervaporation separation processes, this effect is significant.

Coupling transport phenomena can have different origins, including the ones described in section 3, such as membrane thickness, craze defects in thinner membrane,<sup>72</sup> membrane swelling, or plasticization effect. It is noteworthy that coupling effects can relate to the composition of the feed.<sup>79-81</sup> This phenomena has, for example, been observed for bio-based aroma, where compounds are often produced via microbial bioconversion.<sup>82</sup> Raisi et al. studied different groups of aroma compound (3-methylbutanal, isopentyl acetate, n-hexanol, and  $\alpha$ -ionone) mixtures.<sup>83</sup> From binary mixtures, each aroma compound was mixed with de-ionized water to make a dilute aroma/water solution, whereas ternary mixtures included two aroma compounds and de-ionized water. No coupling effects were observed at low aroma concentrations (<200 ppm). The molecules of aroma are separated by a large amount of water in diluted solutions. The interactions among aroma molecules are too small to influence their permeation behavior. Therefore, the coupling effect is not significant at low aroma concentrations. At a higher concentration, coupling effects were observed for 3-methylbutanal/n-hexanol/water and 3-methylbutanal/ $\alpha$ -ionone/water mixtures. In this case, 3-methylbutanal can enhance the permeation of n-hexanol and  $\alpha$ -ionone. In addition, isopentyl acetate showed a strong coupling effect with all aroma compound (3-methylbutanal, n-hexanol, and a-ionone) mixtures. The partial flux of these aromas was increased compared to their binary mixture with water. According to the diffusion-solution model, the sorption of molecules in the polymeric membrane depends on the affinity between the permeants and the membrane materials. The affinity can be expressed using solubility parameters. In this case, the order of solubility parameters of each aroma compound with a PDMS membrane follows the trend: isopentyl acetate>methylebutanal>n-hexanol>water. This indicates that isopentyl acetate and 3-methylbutanal have a high sorption degree in PDMS membranes.<sup>84</sup> As a consequence, the presence of these components in the feed solution results in swelling effects, enhancing the permeation fluxes of n-hexanol and a-ionone through the membrane.



**Figure 4.** Effect of zeolite 13X content on pervaporation separation of 90 wt% aqueous isopropanol mixture for the BAPP–BODA/13X hybrid membranes at 25 °C. Reprinted with permission from Li et al.<sup>91</sup>

Besides, some organic compounds can modify the polymer phase and change the solubility of other organic chemicals.<sup>84</sup> The solubility of n-butanol decreased when other alcohols were also present in the mixture. The formation of clusters of alcohol molecules via hydrogen bonds modifies the polymer phase, reducing the solubility of n-butanol in the polymer material (poly(octyl)methylsiloxane (POMS)).

Free volume also impacts the coupling effects. In the literature, different studies of free volume have been carried out in order to understand the microscopic change of the membrane.<sup>85-88</sup> The relationship between the free volume in polymeric membranes and the transport properties has been studied for different prosuch as gas separation<sup>86,87</sup> or pervaporation cesses, separation.<sup>85,89-91</sup> The free volume within the polymer consists in disordered voids with sizes between 0.1 and 0.5 nm. This is an important factor for the transport of penetrants through polymeric membranes and has a significant influence on the separation of small molecules, such as water or alcohols. Pervaporation involves a contact between the membrane and the liquid feed, which can vary in composition over time. The free volume in the membrane can also change during the process of membrane swelling. A swollen membrane has a much higher free volume than a dry one, therefore, a wetted pervaporation membrane can have a strong effect on the diffusion. In an early study on the effect of a water-swollen poly vinyl alcohol membrane,<sup>88</sup> the expansion of free volume was said to occur in three stages. Initially (concentration of water <8 wt%), the mean size of free volume has no significant change because the water molecules bond to the hydroxyl groups of PVA. With the increase of water concentration up to 30 wt%, the mean radius of free volume started to increase because the water molecules expanded the inter/intra chain distance of PVA. When water concentration reached 30 wt%, the free volume expansion reached its maximum. The change of free volume is reversible. Satvanaravana et al. investigated the free volume size of both water soaked and dried membrane (PERVAP 2210), and it was shown that the size of the free volume is reversible if a dry membrane experienced sorption followed by drying.<sup>92</sup> However, the sorption degree of a used membrane was only partially reversible, which was almost 50% lower than a fresh membrane.

As the expansion of the free volume can reduce the selectivity of pervaporation membranes, one of the most straightforward solutions to solve this issue is to introduce inorganic and rigid particles into the polymer in order to inhibit the expansion of free volume. Li et al. studied the influence of zeolite 13X into a polyimide (BAPP-BODA) membrane.<sup>91</sup> The resulting free volume radius was between the free volumes of pure BAPP-BODA (2.85 Å) and zeolite 13X (4.08 Å). In addition, the number of free volume cavities was reduced after introducing zeolite into the polymer matrix. The free volume radius distribution of the hybrid membrane was within the range of the kinetic radius of water (1.2 Å) and isopropanol (3.86 Å). By introducing zeolite 13X into the polyimide membrane, the expansion of the free volume caused by membrane swelling was significantly reduced. The permeation increases with increasing of the 13X zeolite content into the polyimide membrane, due to the molecular sieving effect and hydrophilicity of the zeolite 13X. However, the separation factor was almost constant in the permeate under 90 wt% aqueous isopropanol mixture (Fig. 4).

A similar study was carried out by Shi *et al.*<sup>90</sup> ZIF-8 (zeolitic imidazolate framework-8) nanoparticles were added into a polybenzimidazole (PBI) membrane for the separation of alcohols and water. The swelling degree of the membrane in the presence of water, methanol, and ethanol solutions was decreased after introducing ZIF-8 particles into the membrane. In addition, the swelling caused by water was subdued significantly because of the hydrophobic properties of ZIF-8 particles. Comparing the performance of PBI membrane with and without ZIF-8 particles, it was observed that ZIF-8 addition can suppress the changes of membrane structures and limit the expansion of free volume, which is otherwise caused by swelling due to ethanol. The free volume diameter of PBI/ZIF-8 membrane (swollen by ethanol) is smaller than that of the PBI membrane (4.9 vs 5.9 Å), leading to a better selectivity for the hybrid membrane.

In some cases, such as in the production of biofuels, the low molecular weight ethanol and butanol must be removed while the aqueous medium of fermentation is retained. In the work of Petzetakis et al.,<sup>89</sup> an artificial free volume inside a cross-linked PDMS membrane was created, based on the self-assembly of polyethylene-b-polydimethylsiloxane-b-polyethylene triblock copolymers (EDE), for purifying ethanol/water and butanol/water mixtures by pervaporation. The experimental results (Fig. 5) showed that the improvement of the permeability of butanol and ethanol is significantly dependent on the amount of artificial free volume, as these alcohols have a larger molecular radius than water. In addition, the selectivity was improved by creating more free volume in the PDMS membrane. The experimental results show that these artificial free volumes formed by self-assembly lead to more hydrophobicity than in cross-linked PDMS. Therefore, the transportation of less polar molecules, such as butanol, is enhanced. One important feature is that the improvement of permeability of EDE/PDMS copolymer membrane does not imply a decrease in selectivity.93,94

### **PERVAPORATION MEMBRANES**

The use of pervaporation separation for bio-based mixtures can be challenging, considering that the complexity of the feed composition leads to the use of multiple separation steps. In recent years, novel membranes have been developed to separate specific bio-based mixtures. Table 1 summarizes the different applications for which pervaporation membranes were used, and the relation of flux and separation factor for typical biomolecules is shown in Fig. 6. The separation processes can be divided into two main categories depending on the nature of the mixture, namely water-organic (dehydration) or organicorganic separation. Dehydration separation involves the separation of water from organic components, including, for example, mixtures of acids, alcohols, esters, and water from esterification reactions. Industrial applications for the removal of water from an organic phase using pervaporation are well-known and documented.<sup>131</sup> For instance, membranes produced by SULZER, PolyAn, have been commercially available for dehydration processes. These commercial membranes, based on polyvinyl alcohol and polyimide materials, can permeate water with high flux and selectivity thanks to their chemical composition and structure, which improve the hydrophilicity of the membranes. The application of pervaporation technology for the separation of organicorganic mixtures is not as developed in the industry.

Generally, membranes can be classified in three groups: organic, inorganic, and inorganic–organic hybrids.

### Organic membranes

Organic membranes, often polymeric, are the membreanes most studied and used in pervaporation. They generally exhibit low mechanical resistance and thermal stability. The trade-off between permeability and selectivity is very common when organic membranes are used. However, they are attractive for many separation processes thanks to their low cost and high flexibility.<sup>23</sup>

The chemical resistance of these membranes can also limit their use for some applications. Some polymer materials seem to be good candidates for a specific separation but cannot be applied in other mixtures because they react with some of the components in the mixture. For instance, polybenzimidazole (PBI) is a good membrane material for pervaporation dehydration, but it has a tendency to form PBI-acid, which limits its application for the separation of acidic mixtures. However, an appropriate



**Figure 5.** Membrane separation permeability and selectivity for butanol and ethanol. (a) Butanol permeability (right ordinate) and ethanol permeability (left ordinate) as a function of artificial free-volume,  $f_{AFV}$ , (bottom ordinate). Blue circles: butanol and red squares: ethanol are introduced EDE in cross-linked PDMS membrane; black circle: butanol and black square: ethanol are permeability by cross-linked PDMS membrane. (b) Butanol/water (left) and ethanol/water (right) selectivity as a function of artificial free-volume  $f_{AFV}$  (bottom ordinate). Blue circles: butanol/water and red squares: ethanol/water are selectivity by EDE membranes; black circle: butanol/water and black square: ethanol/water are selectivity by cross-linked PDMS membrane. Reprinting with permission from Petzetakis et al.<sup>89</sup>

eparation c	of bio-based	chemicals				www	.soci.o	rg			
Ref.	95	96	26	8	66	100	101	102	103	104	105 106
Composition range	Acetic acid: 55–97 wt%	Binary: water. 0–100 wt% Quaternary: acetic acid: 54 wt%, ethanol: 5 wt%, water: 28 wt%,	Acetic acid: 70 wt%	Acetic acid: 75–95 wt%	Acetic acid: 80–95 wt%	Acetic acid: 5–40 wt%	Acetic acid: 70–99 wt%	Acetic acid: 50–95 wt%	Optimal concentration: 85 wt% isopropanol	lsopropanol: 10–40 wt%	lsopropanol: 4 wt% Fthanol: 20 wt%.
Selectivity	5–38	I	2.9–5.7	Ι	I	I	I	Ι	4019	Ι	
Permeance (GPU)	Water: 2000– 2025 000 Acetic acid: 50–		Water: ~4000– 7000 Acetic acid: ~500– 1000		I	I	I	Ι	I	I	
Separation factor	2-24	130–2070	I	144	631	59	359.33- 441	5461		3.5–2	7–3 46–396
h <sup>-1</sup> )		.36	.34	_	ε		.07	2	•	ų	65 17_

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Table 1. The applicat	tion of pervaporation on tl	he separation of liquid mixtures					
Target component	Mixture	Membrane material	Flux (kg $m^{-2}$ $h^{-1}$ )	Separation factor	Permeance (GPU)	Selectivity	Composition range
Acetic acid	Acetic acid water	Polyphenylsulfone (PPSU)	I	2–24	Water: 2000– 2025 000 Acetic acid: 50– 1500	5–38	Acetic acid: 55–97 wt%
	Acetic acid/ethanol/ water/ethyl acetate	ZSM-5 zeolite	1.24–2.36	130–2070	I	I	Binary: water. 0–100 wt% Quaternary: acetic acid: 54 wt%, ethanol: 5 wt%, water: 28 wt%, ethyl acetate: 13 wt%
	Acetic acid water	Polyphenylsulfone-based membranes, modified with silica nanoparticles	0.76-2.34	I	Water: ~4000- 7000 Acetic acid: ~500- 1000	2.9–5.7	Acetic acid: 70 wt%
	Acetic acid water	Polyelectrolytes complex (PEC)/11- phosphotungstic acid hydrate (PW11) hybrid membrane (PEC/ PW11)	0.44	144	I	I	Acetic acid: 75–95 wt%
	Acetic acid water	Composite membranes of sodium alginate active layer and microporous polypropylene substrate	0.653	631	I		Acetic acid: 80–95 wt%
	Acetic acid water	Polycrystalline silicalite membranes ZSM-5 zeolite crystals	0.22	59	I	I	Acetic acid: 5–40 wt%
	Acetic acid/water	Sodium alginate/polyaniline polyion complex membrane	0.04-0.07	359.33- 441	I	I	Acetic acid: 70–99 wt%
Acetic acid	Acetic acid/water	Sulfonated polybenzimidazole membranes	0.207	5461	Ι	I	Acetic acid: 50–95 wt%
lsopropanol	lsopropanol/water	Polybenzoxazole (C-TR-PBO)	0.09	I	Ι	4019	Optimal concentration: 85 wt% isopropanol
	lsopropanol/water	Polyether block amide (PEBA) membranes	0.3–1.3	3.5–2	I	I	lsopropanol: 10–40 wt%
Ethyl tert-butyl ether	lsopropanol/water Ethyl tert-butyl ether/	PEBA/PVDF blend CA-g-PLA copolymers	0.5-0.65 0.01447-	7–3 46–396			lsopropanol: 4 wt% Ethanol: 20 wt%,
Furfural	ethanol Furfural/water	Zn <sub>a</sub> (him)PMPS	0.02177 2.05–2.15	191-195	I	I	ETBE: 80 wt% 
5	Furfural/water	Metal-organic framework ZIF-8	0.67–1.8	17.6–53.3	Ι	~5–15	Furfural: 0.5–6 wt%
	Furfural/water	nanocomposite HTPB-based hydrophobic	0.003-0.022	100–600	I	Ι	Furfural: 1–8 wt%
	Furfural/water	polyurethaneurea membranes Polydimethylsiloxane (PDMS) membrane	5.162	23.9	4395.7 (Furfural)	4.12	Furfural: 0.5–6.5 wt%

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Table 1. Continued								
Target component	Mixture	Membrane material	Flux (kg m <sup>-2</sup> h <sup>-1</sup> )	Separation factor	Permeance (GPU)	Selectivity	Composition range	Ref.
Tetrahydro-furan	THF/water (0.56 wt% water)	Acrylamide and 2-hydroxyethyl methacrvlate blend	0.57	216	I	I	Water: 50–95 wt%	111
Ethyl lactate	Ethyl lactate/ethanol/ lactic acid/water	Commercial membrane PERVAP <sup>®</sup> 2201 (Only conversion reported: Achieve ~90%)	I	Ι	I	I	lnitial concentration: ethanol:lactic acid = 1–3 M ratio	112
	Ethyl lactate/ethanol/ lactic acid/water	Tetraethoxysilane (TEOS)- chitosan hvbrid membrane	~0.05-0.284	~460-700	I	~18–36	Initial concentration: ethanol:lactic acid = 2–4 M fraction	67
	Water/ethanol/ethyl lactate/lactic acid	PERVAP® 2201	~0.2-3	~600	I	I	Water: 13–63 wt% ethanol: 22–11 wt% ethyl acetate: 41–9 wt% lactic acid: 25–17 wt%	113
	Ethyl lactate/water	Surface-modified alumina membrane (Al <sub>2</sub> O <sub>3</sub> )	0.254 (0.6 wt %)	66.9–78.9	I	l	Ethyl lactate: 0.15–0.6 wt%	114
Ethyl propionate	Ethyl propionate/ water	Surface- modified alumina membrane (Al <sub>2</sub> O <sub>3</sub> )	0.343 (0.6 wt %)	106.5–97.3	I	I	Ethyl propionate: 0.15–0.6 wt%	114
Ethyl butyrate	Ethyl butyrate/water	Surface-modified alumina membrane (Al <sub>2</sub> O <sub>3</sub> )	0.377 (0.6 wt %)	120.5– 122.8	I	l	Ethyl butyrate: 0.15–0.6 wt%	114
	Ethyl butyrate/water	Polyether block amide (PEBA) membranes	0.18-0.2	75-160	I	I	Ethyl butyrate: 100–900 ppm	104
n-butyl acetate	n-butyl acetate/ n-butanol/ water	Polyvinyl alcohol (PVA) and chitosan (CS)	~0.683–1.5	~1500- 4800	I		Butyl acetate: 64 wt% Butanol: 30 wt% Water: 6 wt%	64
n-butyl acetate	n-butyl acetate/water	Polyvinyl alcohol (PVA) and chitosan (CS)	~0.4-0.6	27 000 (25 wt% CS)	I	I	Water: 2 wt%	64
Ethylene glycol	Ethylene glycol/water	Poly(vinyl alcohol) (PVA) and a MOF with hydrophilic sulfonic acid group (SO <sub>3</sub> H-MIL-101-Cr) coated by a thin and uniform polydopamine (PD) layer	0.540	2864	I	68.1	Ethylene glycol: 10 wt%	115
	Ethylene glycol/water	PVA and <i>γ</i> - mercaptopropyltrimethoxysilane (MPTMS)	0.067-0.2	50-311	I	I	Ethylene glycol: 80 wt%	116
	Ethylene glycol/water	Chitosan-poly(acrylic acid) polyelectrolyte complex membranes	0.216	105	I	I	Ethylene glycol: 20–90 wt% optimal concentration: 80 wt% EG	117
	Ethylene glycol/water		0.04377	312	I	T	Ethylene glycol: 70–97.5 wt%	118

Table 1. Continued								
Target component	Mixture	Membrane material	Flux (kg m <sup>-2</sup> h <sup>-1</sup> )	Separation factor	Permeance (GPU)	Selectivity	Composition range	Ref.
	Ethylene glycol/water	Poly (vinyl alcohol)/hyperbranched polyester membrane Composite membranes comprising	~0.081- 0.070	196–388	I	I	optimal concentration: 90 wt% EG Ethylene glycol: 80–99.5 wt%	119
Cyclohexane	Ethanol/ cyclohexane	or poyamics and poyuopamics Ethylene- chlorotrifluoro- erhylene	0.45–1.7	15–31	I	Ι	Ethanol: 30 wt% cyclohexane: 69.5 wt%	120
1,3-propanediol	1,3-propanediol/ water	Allylcyclohexylamine functionalized siloxane polymer	0.0055- 0.0058	9–15	I	I	1,3-propanediol: 10 g/L	121
Methyl anthranilate	Flavor compound of concord grapes	Polydimethoxylsiloxane- polycarbonate	0.055-0.102	4-10	I	I	Methyl anthranilate: 20–200 ppm	122
Succinate	Succinic acid/ ethanol/ diethyl succinate/water	GFT-1005 membrane	1-5.8	I	Ι	I	At 80 °C initial concentration: succinic acid: 0.47 mol/L, ehtanol: 3.56 mol/L, diethyl succinate: 4.41 mol/L at 90 °C initial concentration:	123
							succinic acid: 0.5 mol/L, ehtanol: 4.33 mol/L, diethyl succinate: 4.11 mol/L	
Ethyl levulinate	Ethyl levulinate /ethanol/levulinic acid/water	Catalytic composite membrane consists of two layers: the top layer is the catalytic layer coated with SO4 <sup>-2</sup> /ZrO <sub>2</sub> catalyst, the bottom layer is the dense hydroxyethyl cellulose membrane	23	30-65	I	I	lnitial concentration: levulinic acid:ethanol = 1–3 M fraction	124
Xylene	O-xylene/P- xylene	Polyurethane-zeolite composite membranes	0.07–0.46	0.76–1.37	I	I	O-xylene: 0.1–1.0 wt% and 50 wt%	125
Glycerol carbonate	Methanol/DMC/ glycerol/glycerol carbonate	Sulzer membranes: 1255-30, 4155- 40, 1255-50 and 4155-80 Data from optimal conditions of 1255-50 at 45 °C	0.55	13.5	Methanol: 723.6 DMC: 126.4	5.7	Molar fraction: 0.075/0.291/0.193/0.44 in glycerol/ DMC/glycerol carbonate/ methanol	126
Dimethyl carbonate Acetone/butanol/ ethanol (ABE)	Methanol/DMC Acetone/butanol/ ethanol/water	Nano-silica/polydimethylsiloxane Modified silicalite-1 into polydimethylsiloxane (PDMS)	0.702 0.07–0.09	3.97 Acetone/ water: 40–160 ethanol/ water: 20–40		11	DMC: 5–50 wt% Acetone: 5 g/L Ethanol: 1.2 g/L Butanol: 10.0 g/L	127



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modification can improve the stability of organic membranes. For example, Wang *et al.* developed a novel two-step sulfonation modification technique and investigated the performance of their novel membrane of the dehydration of acetic acid.<sup>102</sup> Sulfonated polybenzimidazole (SPBI) is prepared by sulfonation with sulfuric acid followed by a thermal treatment at 450 °C to develop a stable SPBI membrane with a good resistance to acids. By comparing SPBI and PBI membranes with a 50/50 wt% water/acetic acid mixture, the sulfonated PBI membrane (2.5 wt% H<sub>2</sub>SO<sub>4</sub>, 450 °C, 30 s) gave a flux of 168 g/m<sup>2</sup> h with a separation factor of 6631, while the pristine PBI membrane only gave a 100 g/m<sup>2</sup> h flux with a separation factor of 7. With the sulfonated membrane, the separation performance is better than that of conventional distillation or the other polymeric membranes in the literature.

The chemical interaction between the molecules in the mixture and the polymeric membrane material plays an important role in the separation performance. The hydrophilicity of the membrane materials is a critical property for the separation of the target mixture. Typical hydrophilic membrane materials, such as poly vinly alcohol (PVA), cellulose acetate (CA), and chitosan (CS), are favorable to permeate polar solvents, such as water, ethanol, methanol, etc. Therefore, when the mixture contains two opposite polarity (polar and non-polar) chemicals, these membranes can have a good separation performance and polar molecules can diffuse through the membrane preferably. For example, Falbo et al. prepared ECTFE (ethylene chlorotrifluoroethylene) polymeric membranes via thermally induced phase separation (TIPS) technique using N-methyl-2-pyrrolidone as the latent solvent and glycerol triacetate, triethyl citrate, and adipic acid as plasticizers in order to improve polymer processability.<sup>120</sup> It was observed that all the membranes showed a high affinity to polar solvents, especially to ethanol. In addition, a low affinity to non-polar solvents (cyclohexane) was observed. The experiment was carried out by using a binary azeotropic mixture of ethanol and cyclohexane (30.5% w/w and 69.5% w/w) at different temperatures. The experimental results showed that the membranes with triethyl citrate and glycerol triacetate had a higher total flux, 1.7 and 1.5 kg/m<sup>2</sup> h, with an ethanol/cyclohexane selectivity of 15 and 16, respectively.

On the contrary, the hydrophobic membranes were widely applied in the separation of less polar or non-polar molecules. Typical polymer materials are polydimethylsiloxane (PDMS), polyether block aminee (PEBA), and poly(octylmethylsiloxane) (POMS). The application of hydrophobic membranes has a great interest in the separation of aroma compounds.<sup>132</sup> For example, Unlu studied the separation of binary aqueous solutions of the aroma components (propyl acetate, pentyl acetate, and octyl acetate) by using hydrophobic polyvinyl chloride membranes.<sup>133</sup> It was found that the separation factor value for propyl acetate is higher than that of octyl acetate and pentyl acetate, due to its low swelling degree. The flux and separation factor of propyl acetate aqueous mixture were obtained as 1.57 kg/m<sup>2</sup> h and 158, respectively. Although the separation factor of the binary aroma aqueous solution is concentration and temperature dependent (when the temperature and the feed concentration increased, the separation factor decreased), it still can be concluded that the pervaporation is an efficient process for aroma recovery from aqueous solutions and the polyvinyl chloride membrane exhibits good performance for the separation of aroma compounds from water. In addition, a similar principle was applied in the separation of water-methyl t-butyl ether (MTBE) by using hydrophobic membranes polydimethylsiloxane (PDMS).<sup>134</sup> The experimental results show that the water flux

Table 1. Continued								
Target component	Mixture	Membrane material	Flux (kg m <sup>-2</sup> h <sup>-1</sup> )	Separation factor	Permeance (GPU)	Selectivity	Composition range	Ref.
				butanol/				
				wate:				
				35-100				
Pyridine	Pyridine/water	PEBA/Cu <sub>2</sub> O mixed-matrix	0.07-0.12	16–6	I	I	Pyridine: 0.5–2.5 wt%	129
		membranes						
N-methyl pyrrolidone	NMP/water	Nanocomposite PEBA membrane	2.3–5.9	1400–60			Water: 0.5–4.1 wt%	130

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Figure 6. Membrane separation flux vs. separation factor classified as black: organic acid, red: esters, green: ethers, and blue: aromatic organics.

was small and decreased with the increasing of MTBE concentration because it is unfavorable for water molecules to diffuse through the highly hydrophobic membrane.

### Inorganic membranes

Inorganic membranes have a low swelling degree, good mechanical properties, and a good chemical and thermal resistance compared to organic ones. However, they have a higher production cost and are difficult to fabricate as defect-free membranes. The membrane materials zeolite and silica are very common and have been extensively used in the literature.<sup>135</sup> The materials for preparing silica membranes are SiO<sub>2</sub>, SiO<sub>2</sub>—TiO<sub>2</sub>, SiO<sub>2</sub>—ZrO<sub>2</sub>, *etc.* They are stable at high temperatures and in acidic environments. The silica-based membranes prepared by sol–gel processing are highly permeable and selective. This method offers a great advantage for the control of pore sizes.

The application of a silica membrane for pervaporation can be found in the dehydration of alcohols,<sup>136,137</sup> dehydration of acids<sup>138,139</sup> and separation of organic–organic mixtures.<sup>140</sup> The silica membrane exhibits a high and stable water flux (5.4 kg/m<sup>2</sup> h) in isopropyl alcohol (IPA)/water mixture using silica-zirconia membranes with a separation factor 2500 under the condition 10 wt% water in the feed at 75 °C.<sup>136</sup> Silica membranes are promising for the dehydration of acetic acid solutions due to their high stability in contact with acidic solutions. For example, a separation factor of 450 and a water flux of 0.9 kg/m<sup>2</sup>·h can be achieved by a silica membrane with 10 mol% water/acidic acid mixture at 70 °C.<sup>138</sup>

Zeolites are a mixture of silicates-alumina with different compositions of silicon to aluminum ratio. The ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is an important factor for the performance of such inorganic membranes. The zeolites form a crystalline structure and pore size can be around several nanometers. It is found that a low silicon to aluminum ratio can improve the hydrophilicity of the membrane, leading to a preferential sorption of water inside the pores.<sup>141</sup> However, the stability of zeolite membranes in acidic environments is a challenge.<sup>142</sup> The zeolite membranes can be destroyed by the hydrolysis reaction resulting from an acidic environment when Si–O and Al–O bonds in zeolite are dissociated. Furthermore, the silica-alumina layer is dissolved into the solution. Consequently, the zeolite membranes lose their selectivity. Acidstable zeolite membranes are improved by increasing the SiO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub> ratio, therefore, trading off hydrophilicity. For example, ZSM-5 zeolite membranes were studied for the separation of acetic acid/water and acetic acid/ethanol/water/ethyl acetate.<sup>96</sup> It was found that a higher Si/Al ratio can decrease the hydrophilicity of the membrane. However, the acid-stable ZSM-5 membrane still has an acceptable water permeability for target mixtures. The water content in permeates can achieve 99.5 wt% in both binary and quaternary mixtures.<sup>96</sup>

#### Organic-inorganic hybrid membrane

Organic-inorganic hybrid membranes have interesting properties for pervaporation applications, such as their thermal stability, good mechanical properties, and chemical resistance. The major application of hybrid membranes is dehydration. Ma et al.<sup>67</sup> studied organic-inorganic hybrid membranes prepared from the solgel polycondensation of tetraethoxysilane (TEOS) in chitosan (CS) aqueous solution. The membranes were studied for the pervaporation-assisted esterification of lactic acid with ethanol. Chitosan is an interesting bio-based material for the preparation of pervaporation membranes because of its hydrophilicity.<sup>143</sup> On the other hand, its low thermal stability and low mechanical resistance are problematic. By introducing TEOS, the hydrophilicity and thermal stability of such membranes can be improved. The TEOS-CS hybrid membrane gives a high selectivity to water in the separation of aqueous ethanol mixtures. The combination of a batch reactor (reaction between lactic acid and ethanol to produce ethyl acetate and by-product water) and pervaporation with a hydrophilic membrane can shift the equilibrium of the esterification reaction of ethanol and lactic acid, enhancing the yield in ethyl lactate.

For the production of bio-based furfural by xylose dehydration, the performance of  $Zn_2(bim)_4$  (bim = benzimidazolate ion) and PMPS (polymethylphenylsiloxane) hybrid membrane improves the membrane flux and separation factor if compared to pure PMPS, thanks to the presence of  $Zn_2(bim)_4$  crystals.<sup>107</sup> In addition, the presence of  $Zn_2(bim)_4$  reduces the membrane swelling effect while the stability of the material is better than with pure PMPS.

Liu *et al.* made a ZIF-8-silicone membrane on a stainless-steelmesh by using a Plugging-Filling method.<sup>108</sup> In a first plugging step, the ZIF-8 nanoparticles were plugged in HOSSM (hierarchically ordered stainless-steel-mesh). Then, the plugged HOSSM was dip-coated in a solution containing polymethylphenylsiloxane (PMPS), tetraethyl orthosilicate dibutyltin diaurate dissolved in *i*-octane. The membrane shows a high separation performance (53.3 separation factor) for the recovery of furfural (1.0 wt% in water).

Membrane mechanical strength, chemical resistance, and thermal stability in aqueous solutions are major issues for the pervaporation separation application. For instance, poly acrylic acid (PAA), poly vinyl alcohol (PVA), and chitosan are suitable polymeric materials for pervaporation dehydration of alcohols. However, these materials do not have strong mechanical properties and lack stability in aqueous solutions due to their excessive swelling. As a result, the selectivities of these membranes decrease dramatically during the pervaporation separation. Thus, applications for these polymers remain limited.<sup>144–146</sup> Alternative preparation methods need to be carried out. For example, in the preparation of poly benzoxazole membrane, in-situ thermal conversion of hydroxyl-containing polyimide precursors is applied. An aromatic polyimide can be converted into poly benzoxazole through thermal rearrangement between 350 and 500 °C under vacuum or in an inert gas environment.<sup>145</sup>

Supported ionic liquid membranes (SILMs) have also attracted attention for liquid–liquid separation. Ionic liquids can be designed to have both good chemical and thermal stabilities, while their ionic nature generally leads to a negligible vapor pressure.<sup>147</sup> SILMs have been studied widely for gas separation and purification, for instance with SO<sub>2</sub>/CO<sub>2</sub> and for natural gas purification.<sup>148,149</sup> Even if the study of SILMs in pervaporation remains limited, some applications have been targeted using such systems (See Table 2). Compared to dense membranes, SILMs can lead to better mass transfer properties, as the diffusion coefficient in liquids is much higher than in solids.<sup>156</sup> The fundamental information and recent advances in SILMs technology has been reviewed elsewhere.<sup>157,158</sup>

# PERVAPORATION-DISTILLATION HYBRID PROCESSES FOR THE SEPARATION OF LIQUID MIXTURES

Membranes have been widely applied in the chemical industry for purification processes.<sup>159</sup> As one of the membrane separation technologies, pervaporation has often been compared with other purification techniques, such as distillation and liquidliquid extraction. It is a suitable technology for dehydration of product (ethanol, butanol, isopropanol, etc.) or for separating the mixture forming azeotrope with water, such as some esterification reactions. However, a stand-alone pervaporation process is rare because the composition of the permeate may not reach the purity of product or environmental standards required by the industry. In most cases, pervaporation is combined with other processes to improve its overall efficiency. Two major installation configurations could be defined. The first one consists of pervaporation combined with distillation for separation and purification processes. This process is used, for instance, in the purification of ethyl tert-butyl ether (ETBE), an attractive bio-ether used as an additive in bio-fuels. The bio-ETBE can be synthesized from the reaction of bio-ethanol with isobutene over a catalyst, such as Amberlyst 15 (A15).<sup>160</sup> In the production of ETBE, pervaporation plays an important role in breaking the **Table 2.** The application of SILMs via pervaporation for the separation of bio-based chemicals

Mixtures	IL	Supported membranes	Ref.
vinyl buyrate, butanol,	[C <sub>4</sub> MIm][PF <sub>6</sub> ]	PVDF, PTFE,	150–153
butyl butyrate, burytic		PC, Nylon	
acid	[C <sub>8</sub> MIm][PF <sub>6</sub> ]	Nylon	150–153
	[C <sub>4</sub> MIm][PF <sub>4</sub> ]	Nylon	151–153
	[C <sub>8</sub> MIm][PF <sub>4</sub> ]	Nylon	151–153
	[C <sub>4</sub> MIm][NTf <sub>2</sub> ]	Nylon	151,153
	[C <sub>8</sub> MIm][NTf <sub>2</sub> ]	Nylon	151,153
	[C <sub>4</sub> MIm][Cl]	Nylon	152
vinyl acetate, vinyl	[C <sub>4</sub> MIm][PF <sub>6</sub> ]	Nylon	151
propionate, vinyl	[C <sub>8</sub> MIm][PF <sub>6</sub> ]	Nylon	151
butyrate, vinyl laurate,	[C <sub>4</sub> MIm][PF <sub>4</sub> ]	Nylon	154
methyl acetate, methyl	[OMIm][PF <sub>4</sub> ]	Nylon	154
propionate, butyl			
butyrate, ethyl			
decanoate, methanol,			
propanol, butanol,			
1-octanol, acetic acid,			
propionic acid, butyric			
acid, lauric acid			
1-phenylethanol,	[C <sub>4</sub> MIm][PF <sub>6</sub> ]	Nylon	155
1-phenylethyl	[C <sub>8</sub> MIm][PF <sub>6</sub> ]	Nylon	155
propionate, vinyl	[C <sub>4</sub> MIm][PF <sub>4</sub> ]	Nylon	155
propionate and	[C <sub>8</sub> MIm][PF <sub>4</sub> ]	Nylon	155
propionic acid	[C <sub>4</sub> MIm][NTf <sub>2</sub> ]	Nylon	155
	[C <sub>8</sub> MIm][NTf <sub>2</sub> ]	Nylon	155

azeotrope.<sup>161</sup> The elimination of excess of alcohol in the mixture cannot be achieved using a conventional distillation processes and the final ETBE product cannot reach the purity requirements due to the presence of residual alcohol in the product. Pervaporation-distillation process and reactive distillation were compared in the production of ETBE.<sup>162</sup> In the pervaporation distillation process, the purity of ETBE can reach 95.2 wt%. The permeate is enriched with ethanol and is recycled back in the reactor. The purity of ETBE obtained from reactive distillation (97.3 wt%) is higher than pervaporation-distillation process (95.2 wt%). However, the energy consumption of product, which is much lower than reactive distillation (1205 kWh per ton of product). The pervaporation-distillation scheme is shown in Fig. 7.

Butyl acetate can be produced by reacting butanol and methyl acetate via transesterification. Jimenez *et al.* proposed a new process, combining extractive and reactive distillation for the production of butyl acetate.<sup>163</sup> Although this protocol can produce butyl acetate with high purity, the economic analysis showed that it is not profitable due to the high energy consumption of distillation.<sup>164</sup> In the work of Harvianto *et al.*, a reactive distillation combined with pervaporation (using a polyamide-6 membrane) was applied for the production of butyl acetate from the same reagents (Fig. 8).<sup>165,166</sup> The azeotrope of methanol and methyl acetate was broken by pervaporation. The methyl acetate obtained in the pervaporation retentate is redirected to the reactive distillation as a new feed solution. As a result, a high purity of

methyl acetate was recovered for a high conversion. The energy consumption can be reduced by 71% with this process. This is very promising, since the overall cost of the butyl acetate production is reduced.

Figueroa Paredes *et al.* screened commercial membranes for a pervaporation-distillation hybrid process in the separation of methanol and methyl acetate.<sup>167</sup> It was shown that the best commercial membranes were Poly AI TypM1 (produced by PolyAI) and Pervap 2256 (produced by SULZER). Both membranes can permeate methanol and reduce the overall cost of separation under optimal conditions.

As discussed above, a pervaporation-distillation hybrid system presents a decisive advantage in terms of energy consumption when compared to other separation processes. For the separation of azeotropic mixtures, the pervaporation-distillation hybrid has the additional advantage of being able to break azeotropes, since the pervaporation separation is based on the affinity of molecules and membrane materials and diffusion mechanisms instead of a thermodynamic vapor–liquid equilibrium.

Figure 9 shows a novel concept proposed by Fontalvo et al., <sup>168</sup> in which pervaporation is directly integrated in a single distillation column. In this process, a section of packing or trays in a distillation column is replaced by coated ceramic hollow fiber membranes. The permeate is removed from the lumen side of the ceramic membranes. The reboiler provides the energy for the pervaporation separation. Optimal separation of methanol can be achieved using this protocol for the separation of a mixture of organic compounds (MTBE, 1-butene, methanol). It is found that the pervaporation section in the distillation column located at stage 20 gives the largest driving for removing methanol by pervaporation, thanks to its highest activity at this stage. Such a process has several advantages when compared to traditional systems. First, the energy consumption for pervaporation/separation can be reduced greatly. The condensation of vapor during the distillation can release latent heat, which can be supplied to the pervaporation process. Secondly, the vapor and liquid phases are in contact in the pervaporation section. Therefore, the vapor can enhance turbulence in the liquid phase, which can improve the mass and heat transfer between the liquid and the membrane surface. In addition, a lower membrane area is required if compared to the external pervaporation connection scheme. All these advantages can lead to lower energy consumption and reduced membrane costs.

# REACTION-PERVAPORATION HYBRID PROCESSES IN LIQUID MIXTURE SEPARATION

Pervaporation can be combined with a reactor to form a reactionseparation hybrid process. The advantage of such a combination is that one of the products/by-products can be removed by pervaporation. By doing so, an equilibrated reaction is shifted towards the products, thereby improving the yields according the principle of Le Châtelier-Braun. Biobutanol is an important alternative to gasoline or fuel additives due to its higher energy content and low volatility in comparison with bioethanol. Furthermore, current combustion engines can use biobutanol as fuel directly. In the production of biobutanol via fermentation,<sup>169</sup> lignocellulose is a more economical feedstock than sugar-based compounds. However, the presence of a by-product - furfural - in the reaction mixture can reduce the yield because it is the microbial inhibitory compound for fermentation.<sup>170</sup> The pervaporation process in the biobutanol production plays two functions, namely the detoxification and the separation of butanol. In the detoxification process, 94.5% of the furfural produced by SSB (sweet sorghum bagasse) hydrolysed by dilute acetic acid was removed.<sup>169</sup> In addition, the mixture of butanol-acetone-ethanol was separated again by pervaporation. As a result, the pervaporation process was found attractive to the production of biobutanol and biochemical furfural.

Dehydration is a crucial step to purify various types of bio-based products. In a recent study focused on the production of isopropyl lactate, the esterification of lactic acid by iso-propanol was coupled with pervaporation.<sup>15</sup> By removing water through a PVA-PES membrane during the reaction, the conversion of lactic acid was increased from 51% up to 86%. Commercial membranes for pervaporation dehydration are now available in the market and give a good performance on separation processes.<sup>171</sup> For example, the commercial hydrophilic membrane PERVAP 2201 (Sulzer) was used in the synthesis of ethyl acetate via the



Figure 7. Schematic diagram of the pervaporation integrated hybrid process for production of ETBE. Reprinted with permission from Norkobilov et al<sup>162</sup>



Figure 8. A connection of hybrid reactive distillation with high selectivity pervaporation. Reprinted with permission from Harvianto et al.<sup>165</sup>



**Figure 9.** Hybrid distillation–pervaporation system in a single column (a), ceramic hollow fibre membrane packed section in an integrated distillation pervaporation unit (b). Reprinted with permission from Fontalvo et al.<sup>168</sup>

esterification reaction of ethanol and lactic acid. The conversion of lactic acid was much higher than in a conventional reactor because the water was removed selectively and continuously during the reaction, therefore shifting the thermodynamic equilibrium.

Assabumrungrat *et al.* compared the performance of pervaporation (PVA membrane) -reactor operated under continuous stirred tank reactor (CSTR) and plug flow reactor (PFR) for the reaction tert-butyl alcohol (TBA) and ethanol to produce ethyl tert-butyl ether (ETBE) using a zeolite catalyst.<sup>172</sup> Compared with conventional semi-batch reactor, pervaporation-reactor gives better yield due to the selective removal of water from the reaction mixture. The performance of PFR offers a higher yield than CSTR in a wide range of operational conditions.

Feng *et al.* simulated a batch reactor integrated with a pervaporation unit for removing water from esterification mixtures.<sup>173</sup> It was found that a complete conversion of one reactant can be achieved if the second one is in excess. The joint effect of membrane area (*A*), initial volume of reaction mixture (*V*<sub>0</sub>), and membrane permeability ( $\omega$ ) determined the reactor performance. It turns out that the higher the value of  $\omega(A/V_0)$  is, the higher the conversion at a given reaction time is. Hence, low permeability can be obtained by increasing the membrane area. However, when  $\omega(A/V_0) = 1 \text{ h}^{-1}$ , the reactor performance reaches its upper limit. In addition, temperature is an important factor because it influences the reaction rate and membrane permeability.

Commercial membranes have been applied on pervaporationreaction processes. Table 3 shows that the conversions are improved when a pervaporation unit is coupled with the reactor. It is concluded that pervaporation has a distinctive advantage in improving the conversion and that it can have great potential in industrial applications.

Table 5. The application of commercial memoral	nes on pervaporation-rea	cuon nybria processo	25		
Reaction	Catalyst	Membrane	Conversion (Without PV)	Conversion (With PV)	Ref
Lactic acid + ethanol produces	Amberlyst 15	PERVAP 2201	Lactic acid	Lactic acid	112
Ethyl lactate			conversion 0.21	conversion 0.88	
Acetic acid + benzyl alcohol produces benzyl	p-toluene-sulphonic	PERVAP 1005	Acetic acid	Acetic acid	174
acetate	acid		conversion 0.45	conversion 0.6	
Acetic acid + isopropanol produces isopropyl	Amberlyst 15	PERVAP 2201	isopropanol	isopropanol	175
acetate			conversion 0.66	conversion 0.78	
Acrylic acid + n-butanol produces n-Butyl acrylate	Amberlyst 131	PERVAP 2201	Acrylic acid	Acrylic acid	14
			conversion 0.68	conversion 0.96	170
Propionic acid + isopropyl alcohol produces	p-toluene-sulphonic	PERVAP 2201	Acrylic acid	Acrylic acid	176
isopropyl propionate	acid		conversion 0.69	conversion 0.98	177
Methyl ricinoleate + trimethylolpropane produces trimethylolpropane ricinoleate	Lipomod-34P	Polydimethyl siloxane (PDMS) (Medicone)	Methyl ricinoleate conversion 0.41	Methyl ricinoleate conversion 0.88	177
Lactic acid + isopropanol produces isopropyl lactate	Sulphuric acid	PVA-PES (Permionics)	Lactic acid conversion 51%	Lactic acid conversion 86%	15
Propionic acid + isobutyl alcohol produces	Cenoshpere	PVA-PES	Propionic acid	Propionic acid	178
isobutyl propionate	(composed of SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> and Fe <sub>2</sub> O <sub>3</sub> )	(Permionics)	conversion 67%	conversion 88%	
Lactic acid + butanol produces butyl acetate	Sulphuric acid	PVA-PES	Lactic acid	Lactic acid	179
		(Permionics)	conversion 66%	conversion 88%	
Acetic acid + isopropanol produces isopropyl	Amberlyst 15	PERVAP 2201	Acetate acid	Acetate acid	180
acetate			conversion	conversion	
			73.8%	98.8%	

# Table 3. The application of commercial membranes on pervaporation-reaction hybrid processed

### **OUTLOOK AND PERSPECTIVES**

Pervaporation has been known as a promising separation technology of application in the separation of azeotropic mixtures, thermally sensitive compounds (e.g. vitamin C), and organicorganic mixtures, as well as the dehydration and removal of dilute organics from aqueous solutions. In order to achieve high separation efficiency, the pervaporation membrane plays an important role in the separation process. Pervaporation membranes are commercially available in the market, such as those produced by Pervatech or SULZER. In addition, pervaporation has been successfully applied in several cases, such as ethanol dehydration, and more than 90 solvent dehydration processes using pervaporation units in and industrial scale have been installed worldwide, including bio-ethanol dehydration.<sup>181</sup> However, the application of stand-alone pervaporation in bio-based chemical mixtures is still limited.

A stand-alone process means that the pervaporation unit is only responsible for separating the target mixture and it must provide the required permeate purity, flux, and economic viability. Concretely, bio-based mixtures are very complex, which makes the application of stand-alone pervaporation very challenging. A hydrophilic membrane may have a good separation performance on polar/non-polar compounds but have a very poor performance on polar/polar compounds, for example, MTBE/methanol mixture by using modified poly(ether ether ketone) membrane.<sup>182</sup> The state-of-the-art pervaporation separation shown in this review indicates that most products separated from biobased mixtures by pervaporation were unable to achieve a high enough purity/grade for industrial application, and they had a

limited application due to a lack of suitable membranes. Therefore, the wide application of stand-alone pervaporation separation for bio-based mixtures still needs a long time before it can become a reality, although a large amount of membrane development research work is ongoing. On the other hand, hybrid processes of pervaporation combined with other separation processes, such as distillation, have already shown great potential for bio-based mixtures. Many studies (mainly distillationpervaporation hybrid processes) in this field have demonstrated that a hybrid process is more economic than distillation only, considering energy consumption and overall cost. In a hybrid process, the major objective of pervaporation is typically to break azeotropes in the mixture, and in this case, the requirement of membrane selectivity is less important than in stand-alone pervaporation.

Development of novel membranes is a step required to strengthen pervaporation for the separation of bio-based compounds. Currently, membrane development can be categorized into four areas: organic membranes, inorganic membranes, organic-inorganic membranes, and supported ionic liquid membranes (SILMs). Among them, SILMs are very promising for biobased mixture separation because ionic liquids can be designed by combining different cation and anion by modifying both their chemical and physical properties. Hence, designed ionic liquids can have a very good performance in achieving good selectivity toward target components. In addition, only a small amount of ionic liquid is required to fill the membrane pores and ionic liquid recovery for further reuse is not required. Due to their negligible vapor pressure and high viscosity, ionic liquids in SILMs can provide a stable separation process.

# CONCLUSIONS

The application of pervaporation on the separation of liquid mixtures has been studied extensively and commercial membranes are now available in the market for industrial applications. The most prominent example is dehydration. Many examples in the literature show the great potential of pervaporation for the separation or purification of bio-based products. In the case of dehydration, for example, the mixtures from esterification and fermentation reactions, commercial membranes are available.

In addition, pervaporation can be a good alternative solution for breaking azeotropic mixtures, since the separation mechanism of pervaporation is only dependent on the molecule-molecule interaction and the molecule-membrane materials interaction, regardless of the thermodynamic equilibrium.

Nevertheless, the development of novel membranes is key for the success of the purification of bio-based chemicals via pervaporation. The use of organic–inorganic hybrid membranes is one of the most attractive solutions, since it carries the advantages of both organic and inorganic membranes. They have a better chemical and thermal stability than organic membranes. In addition, a pervaporation-distillation hybrid system can lead to a reduction in energy consumption during the separation process, when compared to distillation, and is also a good alternative for the separation of azeotrope mixtures. A better conversion can be achieved by reaction-pervaporation hybrid processes in the liquid mixture separation.

### **FUNDING**

This research project was supported by the European Regional Development Fund (ERDF) and Wallonia, within the framework of the program operational 'Wallonie-2020.EU'. The authors acknowledge the "Fonds européen de développement régional" (FEDER) as well as the Wallonia (Belgium) for their financial supports via the 'INTENSE4CHEM' (Flow4Syn) project (project N° 699993–152208).

# **CONFLICTS OF INTEREST**

The funders had no role in the design of the study, in the collection, analyses, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.

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