Relation between permeate pressure and operational parameters in VOC/nitrogen separation by a PDMS composite membrane

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ABSTRACT

Transmembrane driving force, which can be produced by permeate pressure, is a significant element in the design of VOC/nitrogen separation processes. Studies on the impart of the pressure on the membrane performance and the separation mechanism can provide important information for the design of new membranes and separation processes. In this work, the effect of permeate pressure on membrane performance was studied for the separation of a cyclohexane/nitrogen mixture using a polydimethylsiloxane (PDMS)/polyamide (PA) composite membrane. The changing trends of the separation performance for the separation of VOCs with different saturated vapor pressures under different permeate pressures were analyzed. The variation in the transmembrane driving force for cyclohexane and nitrogen with different parameters, such as membrane thickness, were also investigated under various permeate pressures. The reason for the decrease in selectivity with increasing permeate pressure was discussed. It was demonstrated that permeate pressure affects the membrane performance mainly by weakening the cyclohexane flux, while having little influence on the nitrogen flux in the studied range due to their different saturated vapor pressures. Lastly, the energy consumption for the VOC/nitrogen separation, which provides fundamental insight for industrial membrane-based VOC recovery, was simulated keeping in consideration all the obtained experimental data.

1. Introduction

Volatile organic compounds (VOCs) are commonly used in industrial applications and may be released into the atmosphere, causing wastage of resources and great harm to both humans and the environment [1-3]. For this reason, governments and institutions have enacted laws and regulations to limit VOC emissions [4]. Several technologies, such as condensation [5], adsorption [6], membrane separation [7], incineration [8] have been developed to tackle the problem. Among them, membrane separation (for example, gas/vapor separation), has been considered as one of the most promising technologies for VOC recovery, because of their advantages such as high recovery rate, no secondary pollution, low energy consumption, small footprint and simple operative processes [4,7,9].

The membrane-based gas/vapor separation is based on a difference in transport rate of the VOCs and nitrogen through the membrane. The transportation is driven by the chemical potential difference (driving force). This means that the membrane plays a key role; it should favor the transportation of VOCs and exclude that of nitrogen in order to achieve excellent separation performance. Consequently, the development of new membrane materials has always been a research hotspot in the past few decades. Polymer membrane materials such as polydimethylsiloxane (PDMS) have been widely studied and industrialized by our group, owing to their easy membrane-forming properties, low cost, and acceptable separation factor [9,10]. Along with that, the easy modification of PDMS made it one of the most studied materials in many other fields, such as microfluidic, biomedical devices and others [11] and this is the reason why PDMS membranes were used in the study.

The driving force can significantly affect the membrane performance [12]. However, when studied in previous works, it was mainly used to calculate permeance or permeability for a consistent comparison [13], without considering the source. The driving force can be produced by several sources, such as vacuum (permeate pressure), sweep gas, and feed pressure [14]. Sweep gas is not typically recommended for the separation of VOCs/nitrogen mixture, because it can dilute the permeated VOCs concentration, increasing the energy required for

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condensation and recovery. Either vacuum or feed pressure are better choices for saving costs. However, the impact of feed and permeate pressure on membrane performance is not thoroughly studied, especially in the context of separation of VOCs and nitrogen mixtures. Huang et al. [15] reported that the optimization of the membrane performance depends mainly on the operating parameters, such as the pressure. Therefore, a deeper understanding of the effects of permeate and feed pressure on membrane performance is crucial. It should also be considered that the evaluation of membrane performance for the separation of VOC/nitrogen mixtures is typically conducted with vacuum downstream. The effect of permeate pressure was first studied considering the separation of cyclohexane/nitrogen mixtures using PDMS composite membranes with various thicknesses.

Under different permeate pressures, the membrane performance can also be influenced by other factors, such as membrane thickness, temperature, and saturated vapor pressure. The changing trends of these parameters with the permeate pressure should also be studied to provide an overall investigation of the separation process, and to offer fundamental data for the potential industrial applications. In this work, the effect of permeate pressure on membrane performance was thoroughly investigated, and the obtained fundamental data are intended to provide great insight for the module design [16]. The effects of various parameters such as feed concentration and temperature on the membrane performance were studied under different permeate pressures and their intrinsic mechanism was also assessed. Different VOCs were used to study the influence of saturated vapor pressure on membrane performance and the energy consumption for the separation of VOC/nitrogen mixture was simulated using the Aspen software.

2. Experiment

2.1. Materials and characterization

Nitrogen (greater than 99.99%) was prepared using an air compressor (AE-11A screw compressors, HANBELL, China). Cyclohexane, methylcyclohexane, and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All chemical reagents used in this experiment were of analytical grade and were used without further purification. The true density of the homogeneous PDMS membrane was analyzed using a TA-2200 true density analyzer (Beijing Builder Electronic Technology Co., Ltd, China).

2.2. Membrane preparation

A PDMS/polyamide(PA) composite membrane was prepared in our laboratory [17], where PDMS polymer (RTV 615) was added in the heptane solution to form a 5 wt% membrane solution, which was stirred at 70 °C for a certain time to reach a viscosity of 90 mPa-s. Then, the membrane solution was coated on a 0.11 μm polyamide substrate using a casting knife to form a composite membrane, which was left overnight to evaporate heptane at room temperature followed by drying at 80 °C in an oven for more than 8 h.

2.3. Gas/vapor separation

A schematic of the experimental setup is shown in Fig. 1. A stream of pure nitrogen was introduced into the VOC liquid tanker to generate a saturated VOC/N2 mixture stream, which was combined with another stream of pure nitrogen to produce the required concentration of VOC/N2 mixture, with the flow rate being controlled by the ratio of the flow rates of the two pure N2 streams. The blended VOC/N2 mixture then enters the membrane cell for separation. The membrane area was 10.173 cm2. The feed and residual gas concentrations were measured using gas chromatography (GC-2014, SHIMADZU). The permeate pressure was maintained under the desired conditions using a vacuum pump (D8C, LEYBOLD), and it remained constant over a period of time. The permeate VOC was collected through a cold trip and then weighed using a digital balance.

2.4. Analytical method

The separation performance of the PDMS composite membrane was measured using a modified constant volume/variable pressure method [18]. Permeation flux (J), permeability, and selectivity were used in the expression of membrane performance. The permeation flux was calculated using the following formula:

\[ J = \frac{W}{At} \]

where W is the weight of the permeating component, A is the membrane area, and t is the time.

The intrinsic properties of the membrane can be expressed by permeability P, which is calculated as follows:

\[ P = \frac{JL}{X_{\text{feed}}P_{\text{feed}} - X_{\text{perm}}P_{\text{perm}}} \]

where \( P_{\text{feed}} \) and \( P_{\text{perm}} \) are the feed and permeate pressures, respectively, \( L \) is the thickness of the PDMS layer, and \( X_{\text{feed}} \) and \( X_{\text{perm}} \) are the molar concentrations of component \( i \) on the feed and permeate sides, respectively.

The permeability of the permeating component is determined by the following equation [19]:

---

Fig. 1. Schematic diagram of the experimental setup for gas/vapor separation.
\[
p_i = \frac{L273Vdp}{A(\chi_{\text{feed}}P_{\text{feed}} - \chi_{\text{perm}}P_{\text{perm}})T/T_{\text{ref}}}
\]  

(3)

where \(L\) is the thickness of the PDMS layer, \(\chi_{\text{feed}}\) and \(\chi_{\text{perm}}\) are the molar concentrations of component \(i\) on the feed and permeate sides, \(J_i\) is the flux of component \(i\), and \(dP_i/dt\) is the increment of the pressure of \(i\) at time \(T\) in the permeate.

The concentration of the mixture at the permeation side can be determined by closing valve \(B\) and measuring the pressure over time [20,21]. Selectivity(\(\alpha\)) is calculated as follows:

\[
\alpha = \frac{P_{\text{voc}}}{P_{\text{N2}}}
\]

(4)

where \(P_{\text{voc}}\) are permeability of VOC, \(P_{\text{N2}}\) are permeability of \(\text{N}_2\).

2.5. Simulation of energy consumption

The Peng-Robinson equation of state in Aspen Plus software (Aspen Tech) was employed to calculate the thermodynamic parameters of the separated mixtures [22,23]. During the actual experiments, the membrane selectivity varied with the permeate pressure, and a regression equation (\(\gamma = A\exp(B)\)) was employed to fit the selectivity-permeate pressure trend. The degree of consistency between the predicted and experimental data was acceptable, since \(R^2\) was higher than 97%. The regression equation was then implemented in the ACM model on the basis of the experimental and semi-empirical functions reported in our previous work in order to simulate the separation of VOC/nitrogen mixture under different permeate pressures [24]. The simulated conditions were controlled as follows: feed flow rate 100 Nm\(^3\) h\(^{-1}\), temperature 30 \(^\circ\)C, feed pressure 0 kPa, and feed concentration 1 mol%. The flowsheets pertaining to the condensation of the permeates located after the vacuum pump were simulated because under actual conditions, the condensation of the permeate under low permeate pressure is difficult.

For the simulation of the vacuum pump, the compressor module (Compr) was used, and the compression process was assumed to be an isentropic compression process. The ideal isentropic power of the claw vacuum pump is calculated as follows [24,25]:

\[
P_k = \frac{k}{k-1} \frac{1}{\dot{V}_n a_n} \left[ \frac{P_{\text{out}}}{P_{\text{in}}} \right]^{1-1}
\]

(5)

where \(k\) is the isentropic exponent, \(P_k\) is the isentropic power, \(\dot{V}_n a_n\) represents the volume of vapor in the vacuum pump, and \(P_{\text{in}}\) and \(P_{\text{out}}\) represent the pressures of import and export, respectively.

During the working process of the vacuum pump, a large amount of heat is generated due to gas compression. Thus, the process water was used to cool the vacuum pump and maintain its outlet temperature at 30 \(^\circ\)C. This is generally regarded as an ordinary heat exchange process and the enthalpy change of non-condensable gas, \(H_{\text{coolant}}\) is the latent heat of vaporization of VOCs.

3. Results and discussion

3.1. Effect of membrane thickness

It is widely reported that a thin membrane generally leads to high flux under a certain permeate pressure, because of low transport resistance. Our results displayed in Fig. 2 (a) and (b) also show a similar trend. However, when the partial pressure difference (driving force) is used to calculate the permeability of nitrogen and cyclohexane, the trend of the permeability versus the membrane thickness is opposite to that observed for the flux: a higher membrane thickness leads to slightly higher cyclohexane and nitrogen permeabilities, as shown in Fig. 2(c) and (d). This phenomenon was attributed to the alteration of the free volume with the increase of the membrane thickness, because the morphology of structure of the synthesized membranes (amorphous in this case) was not significantly affected by the membrane thickness, as previous reported [17]. Furthermore, other reports [22,24] showed that the impact of free volume on permeability was much higher than membrane crystallinity. Shishatskii et al. [26] reported the decrease in fractional free volume of the membrane with the decrease of its thickness. Our results, shown in Fig. 3, demonstrate a higher density for thinner membranes, which typically translates into a lower free volume [27]. This means that fewer channels and adsorption sites would be available for the transportation of cyclohexane and nitrogen through the membrane, thereby lowering their permeability.

Fig. 2(a) shows that as the permeate pressure increases, the cyclohexane flux decreases, and this is attributed to the reduction of the partial pressure difference of cyclohexane, as shown in Fig. 4. Regarding the nitrogen flux, although the permeate pressure significantly increases (from approximately 200 Pa to 4000 Pa), the relatively high partial feed pressure leads to a slight decrease in the partial pressure difference in comparison with the permeate pressure, this theoretically can weaken nitrogen flux. However, the reduction of the cyclohexane flux means that there is more space available for nitrogen diffusion. These two opposite behaviors compensate each other, leading to almost constant nitrogen flux (Fig. 2(b)). These results also suggest that the sensitivity of the separated species with high saturated vapor pressure is lower compared to that with low saturated vapor pressure [28]. Fig. 2(c) shows that the cyclohexane permeability decreases almost linearly with increasing permeate pressure because of the lower driving force with higher permeate pressure. The lower permeability of cyclohexane implies less cyclohexane transport through the membrane and availability of more space for nitrogen transportation, thereby resulting in a slightly higher nitrogen permeability, as shown in Fig. 2(d).

Fig. 5 shows that the selectivity decreases with increasing permeate pressure because of the simultaneous reduction of the cyclohexane permeability and the slightly increase of the nitrogen one. While the selectivity seems being independent from the membrane thickness, this is because that the morphology of the membrane used in this study is homogenous [17], so the selectivity should be independent from the membrane thickness [29]. Our final conclusion, as possible to evaluate from Figs. 2 and 5, is that high permeate pressure is not good for improvement of the membrane selectivity and permeability. At the same time, the permeate pressure affects the membrane performance by exerting a significant influence on cyclohexane permeability, rather than on the nitrogen one.

In the gas/vapor separation, the partial pressure difference (\(\Delta P\)) of the separated species produces transmembrane driving force, which induces the transport of the separated species through the membrane. While, the membrane is resistant for the transportation of separated species, and this resistance is proportional to its thickness. Therefore, a minimum \(\Delta P\) for the transportation of the separated species should
exist for a membrane with a certain thickness, and this will provide a guide for the selection of operational conditions for the separation. The cyclohexane flux for different membrane thicknesses at different $\Delta P$ values (which can be obtained by changing the permeate pressure) was herein studied, as shown in Fig. 6 (a). A linear relationship between the cyclohexane flux and $\Delta P$ can be observed, which shows that when the difference in partial pressure decreases, the transmembrane driving force also decreases and so the flux. Furthermore, if the cyclohexane flux reaches zero, a minimum $\Delta P$ can be obtained. This can also be related to the membrane thickness, because the permeation resistance improves with its increase [30]. A higher membrane thickness leads to a higher $\Delta P$, specifically, from 1.71 kPa for a 1 $\mu$m thick membrane, to 2.03 kPa, for a 1.9 $\mu$m thick one. Fig. 6(b) shows the relationship between the nitrogen flux and $\Delta P$; a similar trend can be observed: the higher the $\Delta P$, the higher the flux. However, the minimum $\Delta P$ of nitrogen transportation is much higher compared to the one of cyclohexane transportation. These results suggest that the PDMS membrane is dense and without defects. The low affinity between nitrogen and PDMS membrane is also responsible for the limited adsorption and diffusion of nitrogen through the membrane; thus, high selectivity can be observed in the separation of VOCs from the nitrogen.

3.2. Effect of VOCs with different saturated vapor pressure

As anticipated, the permeate pressure has a lower influence on the
permeability of a compound with high saturated vapor pressure, this is demonstrated by the sharply decrease of the flux with the increase of the permeate pressure. To further validate this result, VOCs with different saturated vapor pressures, but similar other properties, such as solubility parameters and molecular kinetic diameter, were chosen for comparison in this separation (Table 1). It can be evaluated from Fig. 7(a) and (b), that the flux and changing range of permeability of the VOC with low saturated vapor pressure is, indeed, larger than the correspondent with high saturated vapor pressure. With the increase in permeate pressure, the flux gap between the VOCs is gradually narrowed. When the regression equation ($y = 1/(a \times x + b)$) is used to simulate the VOC flux or the permeability changing trend with permeate pressure, they tend to become flat and constant and this is attributable to the decrease of the partial pressure difference (Fig. 7(a) and (b)). This phenomenon suggests that a high permeate pressure weakens the effect of VOC properties on membrane performance. On the other hand, when the permeate pressure is higher than 6 kPa, its effect on membrane performance for the separation of VOC/nitrogen can be neglected. These observations provide fundamental data for the optimum energy consumption for gas/vapor separation.

Fig. 7(c) and (d) shows lower nitrogen flux and permeability in the separation of VOC/nitrogen mixture, compared to the permeation of pure nitrogen. This phenomenon occurs because VOC has a higher affinity for the membrane, which favors its preferential adsorption in the membrane to occupy the delivery channels. The kinetic diameter of VOC is large and its diffusion rate is low, which hampers the permeation of nitrogen through the membrane [9]. Thus, a lower nitrogen flux and permeability is observed in the separation of VOC/nitrogen mixture, especially compared to the pure nitrogen permeation. Fig. 7(c) and (d) also show that with increasing permeate pressure, the pure nitrogen permeation decreases slightly because of the slight reduction of the partial pressure difference, as also shown in Fig. 4. The limited increase in nitrogen permeability (and the almost constant flux) with the increase of the permeate pressure in the separation of cyclohexane/nitrogen mixtures, is also consistent with the results shown in Fig. 2(b) and (d).

From Fig. 7, it can also been seen that the VOC with low saturated vapor pressure shows a high flux or permeability, because of its high condensability, which is consistent with previous studies [18]. Therefore, a higher selectivity can be observed, as shown in Fig. 8. In addition, the selectivity decreases with the increasing permeate pressure, owing to the reduced VOC permeability and a slightly higher nitrogen one.

Fig. 9 shows the effects of partial pressure difference ($\Delta P$) on VOC flux. It can be seen that the bigger the partial pressure difference, the higher the driving force, and consequently, a higher VOC flux was observed. This means that more VOC can be pushed through the membrane. However, under same partial pressure difference, lower saturated vapor pressure of VOC exhibits (relatively) higher flux and this may hint that a low VOC saturated vapor pressure is beneficial for its condensation in the membrane. A high condensability favors the adsorption of VOC on the membrane surface and, therefore, its transport of VOC through the membrane, resulting in high flux, because in the permeation of VOC through the membrane, the adsorption is the rate-limiting step. This also suggests that under similar solubility parameters and same feed concentration, condensability is the key factor in determining the transportation of VOC thorough the membrane.

![Fig. 5. Cyclohexane/nitrogen selectivity versus permeate pressure.](image-url)

![Fig. 6. Relationship between the flux of cyclohexane (a) and nitrogen (b) and the difference in partial pressures created by changing permeate pressure [feed VOC concentration is 4%, feed pressure is 0 kPa (feed gauge pressure) at 30 °C, and flow rate is 3 L.min⁻¹].](image-url)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Solubility parameter(Mpa¹/²)</th>
<th>Molecular weight (g mol⁻¹)</th>
<th>Kinetic diameter(Å)</th>
<th>Saturated vapor pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>18.2</td>
<td>92.14</td>
<td>5.85 [31]</td>
<td>4.89</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>C₇H₁₄</td>
<td>15.9</td>
<td>98.19</td>
<td>6.0 [32]</td>
<td>5.33</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C₆H₁₂</td>
<td>16.7</td>
<td>84.16</td>
<td>6.0 [31]</td>
<td>16.2</td>
</tr>
<tr>
<td>PDMS</td>
<td></td>
<td>14.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

VOC: volatile organic compound; PDMS: polydimethylsiloxane.
3.3. Effect of feed cyclohexane concentration

Fig. 10 displays the flux and the permeability of cyclohexane and nitrogen for the separation of their mixtures at different feed cyclohexane concentrations and permeate pressures. It is evident in Fig. 10(a) that a high feed cyclohexane concentration indicates a high probability for its molecules to come in contact and get adsorbed into the membrane, leading to a high flux. When the permeate pressure is 4 kPa, there is a distinct linearity between the cyclohexane flux and feed concentration, which indicates a negligible swelling phenomenon in the membrane. These results also indirectly imply the long-term stability of the membrane, as shown in Fig. 11; during the 300 days measurement, the PDMS selective layer tightly anchors to the substrate because of the negligible swelling. If the swelling is strong, the frequent switching of vacuum pump under experimental conditions may lead to the peel-off of the PDMS selective layer from the substrate and, eventually, to the breaking of the membrane.

With decreasing permeate pressure, a higher driving force is produced on both sides of the membrane so that more cyclohexane molecules can be adsorbed to swell membrane, improving the cyclohexane flux and, gradually, linear relationship between the cyclohexane flux and feed cyclohexane concentration starts deviating from each other. In other words, the higher the feed cyclohexane concentration, the greater the change in flux with permeate pressure because of the stronger
swelling phenomenon. With increasing cyclohexane flux, more transport channels are occupied by the large cyclohexane molecules, hindering the nitrogen transportation and leading to a lower nitrogen flux. The permeabilities show similar trends, as shown in Fig. 10 (c) and (d). The increase of the cyclohexane permeability along with the decrease of the nitrogen permeability with feed cyclohexane concentration resulted in a higher selectivity, as shown in Fig. 12.

Fig. 13 shows the changing trend of the cyclohexane flux with the partial pressure difference. Obviously, a higher partial pressure difference leads to a higher cyclohexane flux, because of the increased driving force. Under the same partial pressure difference, the lower feed cyclohexane concentration shows a higher cyclohexane flux. This can be ascribed to the condensability of the cyclohexane, because of its higher vapor concentration, it is more likely to be condensed in the pores or on the membrane surface via capillary condensation [33,34], thereby resulting in the molecular aggregation of cyclohexane and a lower diffusion coefficient. Lue et al. [35] also observed similar results, finding that the diffusion coefficient depends on the feed vapor concentration and a higher feed concentration leads to a lower diffusion coefficient. Therefore, the vapor has much higher permeability than the liquid [34]. This also results in a higher minimum partial pressure difference ($\Delta P$).
3.4. Effect of feed temperature

Besides pressure, permeability is also a function of temperature [17,18], which can be described using the Arrhenius equation:

\[
p = p_0 \exp \left( \frac{-E + \Delta H}{RT} \right)
\]

where \( p \) is the permeability, and \( p_0, R, \) and \( T \) are the pre-exponential factor, universal gas constant, and temperature in kelvin, respectively. The value of \( E + \Delta H \) \( (E \) and \( \Delta H \) are the activation energy and heat of the gas solution, respectively) provides the activation energy of the permeation, which can be obtained from the slope of the ln \( P \) versus 1/T plot shown in Fig. 14. The negative value indicates the dominance of the solubility of cyclohexane in its transportation through the membrane, because the diffusion activation energy is usually positive, whereas the heat of the solution is generally negative, which is in consistency with previously reported studies [18]. When the permeate pressure increases, the diffusion resistance (or diffusion activation energy) increases too, due to the decreasing driving force. The heat of the solution, instead, is generally constant in regard to the change in permeate pressure. Lastly, the value of the activation energy gradually tends to become positive, as shown in Fig. 14(a). This phenomenon is supposed to be valid for the permeation activation energy of nitrogen too. However, as shown in Fig. 14(b), the activation energy decreases with increasing permeate pressure. This may be explained by two reasons: first, the partial pressure difference of nitrogen (Fig. 4) slightly changes with the permeate pressure, and this may lead to a subtle variation of the diffusion coefficient. Second, in the VOC/nitrogen mixture separation, the more permeable cyclohexane can occupy the transporting channels, thus, blocking the nitrogen permeation through the membrane and resulting in a lower nitrogen flux. With the increase of the permeate pressure, fewer cyclohexane molecules can permeate through the membrane and more space becomes available for nitrogen transportation, (as already discussed), eventually leading to a lower diffusion coefficient at a higher permeate pressure, and a lower permeation activation energy with higher permeate pressure can thus be observed.

Fig. 15 shows the flux and the permeability of cyclohexane and nitrogen in their separation at different permeate pressures and temperatures. It is clear from Fig. 15(a), that a higher temperature leads to a lower cyclohexane flux because the adsorption (the rate-limiting step), due to the exothermic nature of the sorption process, reduces the cyclohexane adsorption on the membrane with the increase of the temperature [36]. Conversely, for nitrogen, the diffusion step is the dominating factor. Increasing the temperature enhances the thermal motion of PDMS polymer segments and, as a result, reduces the transportation resistance through the membrane. A higher nitrogen flux is thus observed at a higher temperature, as shown in Fig. 15(b). In addition, Fig. 15(a) and (b) also show that a high permeate pressure generally results in a low cyclohexane flux, but a high nitrogen one. The permeability (Fig. 15(c) and (d)) displays similar trends, because of the competing relationship between cyclohexane and nitrogen [9] that leads to a reduction of the selectivity (Fig. 16).

3.5. Variation in energy consumption with permeate pressure

As thoroughly discussed, a high permeate pressure results in low separation performance, since the sensitivity of VOC flux by permeate pressure is greater than that of nitrogen flux. However, it is impractical to apply the experimental low permeate pressure conditions in the industry. In order to study the trend in energy consumption with the permeate pressure, the energy simulation of the separation of VOC/nitrogen mixture was performed using Aspen Plus software.

Fig. 17 shows the energy consumption of the separation of VOC/nitrogen mixtures under different permeate pressures, which implies that the VOC with low saturated vapor pressure needs more energy for separation than that with high saturated one, because of the more difficult condensability of the former. Both low and high permeate
Pressures do not favor a decrease in the energy consumption of vacuum pump if a dry vacuum pump is used, because under a low permeate pressure, much of the pump energy is used to compress the permeate, and a permeate with a higher compression ratio consumes more energy. Furthermore, the compression process generates heat and cooling is necessary to avoid overheating, which also leads to a higher energy consumption. Therefore, the lower the permeate pressure, the higher the energy consumption of both vacuum pump and pump cooling. When the permeate pressure increases, the membrane selectivity decreases, implying that more nitrogen is transported through the membrane. This leads to a more difficult liquefaction at high pressure. Because of that, a larger volume of gas volume needs to be compressed, resulting in a higher energy consumption of vacuum pump and pump cooling. For condensation, the energy consumption increases with the permeate pressure because a high permeate pressure leads to a low selectivity and a low concentration of the permeate. Accordingly, more energy will be needed to obtain the same liquefied VOC solution. So, we concluded that the optimum permeate pressure for the separation of VOC/nitrogen mixture under experimental conditions, falls in the range of 1–5 kPa if a dry claw vacuum pump is used.

4. Conclusions

In this work, the effect of permeate pressure on membrane performance at different temperatures, feed concentrations, pressures, and other factors was thoroughly studied. The results showed that a high membrane thickness generally results in a lower flux but a higher permeability. Regarding the change in flux with the change of the permeate pressure, the sensitivity of the separated species with a high saturated vapor pressure is lower than the correspondent with a low pressure. Under the same partial pressure difference, a low feed cyclohexane concentration was found to be beneficial for the permeation of cyclohexane through the membrane. The presence of cyclohexane can hamper the transportation of nitrogen, resulting in a low nitrogen flux (or permeability) and to an overall increase of the selectivity. It was found that the temperature affects cyclohexane adsorption in the membrane, weakening its flux and permeability. On the other hand, it increases the nitrogen flux and its permeability, indicating different rate-limiting steps. In summary, these results can provide references for future explanation of membrane separation mechanisms. In addition, an optimum energy consumption under the permeate pressure range ~1–5 kPa in the separation of VOC/nitrogen mixtures with different...
properties was deduced, this provides a significant foundation for the future design of the membrane separation process.

**CRediT authorship contribution statement**

Bowen Shen: Methodology, Investigation, Writing – original draft, Investigation. Shuai Zhao: Methodology, Investigation, Writing – original draft. Xiaoquan Yang: Methodology, Investigation, Writing – original draft. Mariolino Carta: Writing – review & editing. Haoli Zhou: Conceptualization, Supervision, Writing – review & editing. Wanqin Jin: Supervision, Writing – review & editing.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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