

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

Bowen Shen ^a, Shuai Zhao ^a, Xiaoquan Yang ^a, Mariolino Carta ^b, Haoli Zhou ^{a,*}, Wanqin Jin ^a

^a State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, 5 Ximofan Road, Nanjing 210009, PR China

* Corresponding author: E-mail: zhouhl@njtech.edu.cn

Tel: +86-25-83172272, Fax: +86-25-83172272

^b Department of Chemistry, Swansea University, College of Science, Grove Building, Singleton Park, Swansea, SA2 8PP, UK.

Abstract:

Transmembrane driving force, which can be produced by the effect of the permeate pressure, is a significant element in the design of VOC/nitrogen separation processes. Studies on the impact of this pressure on the performance and the separation mechanism can provide important information for the design of new membranes and separation processes. This work reports the study of the effect of permeate pressure on the performance of a polydimethylsiloxane (PDMS)/polyamide (PA) composite membrane, aiming to improve the VOC/nitrogen separation. The changing trends with different saturated vapor pressures were analyzed according to the change in the permeate pressures for several VOCs. The variation in the transmembrane driving force for cyclohexane and nitrogen was also investigated, considering different parameters such as thickness, temperature and saturated vapor pressure. It was demonstrated that the decrease of the membrane performance was due to the reduction of the selectivity with the increase of the permeate pressure. This was attributed to the effect that the latter has on the VOC flux, which is reduced while the nitrogen flux is maintained. 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.

Keywords: Permeate pressure; PDMS membrane; Volatile organic compound/nitrogen separation; Energy consumption

1. Introduction

Volatile organic compounds (VOCs) are commonly used in industrial applications and, when released into the atmosphere, they can cause 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, especially because of their advantages such as high recovery rate, no secondary pollution, low energy consumption, small footprint and simple operative processes [4, 7, 9].

In gas/vapors, the separation is obtained and tuned by the difference in permeability and selectivity of the VOCs and nitrogen. The transportation (or diffusion) is driven by the chemical potential difference (driving force). This means that the membrane plays a key role when it favors the permeation of VOCs and the exclusion of nitrogen, improving the selectivity and achieving an 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 developed by our group, owing to their ease of formation and processing, their low cost and the reasonable selectivity towards different gas pairs [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 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 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.

Different methods of producing the driving force may result in different operational costs for the industry. For example, the energy consumption for the production of 100 kPa permeate pressure by a vacuum pump, is much higher than that for the production of 100 kPa feed pressure. In view of that, the study the effect that the driving force has on the optimization of operating processes, will prove beneficial, not only, for the improvement of the membrane performance, but also to decrease the operational costs. It should also be considered that the evaluation of membrane performance for the separation of VOC/nitrogen mixtures is typically conducted with vacuum downstream, and this can also significantly affect the membrane performance [12, 22]. The effect of permeate pressure was first studied considering the separation of cyclohexane/nitrogen mixtures using PDMS composite membranes of 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 against the shift of the permeate pressure, should also be studied to provide an overall investigation of the separation process, and to offer fundamental data from the perspective of 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 (>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 TD-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 5wt% 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 $^{\circ}\text{C}$ 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 trap and then weighed using a digital balance.

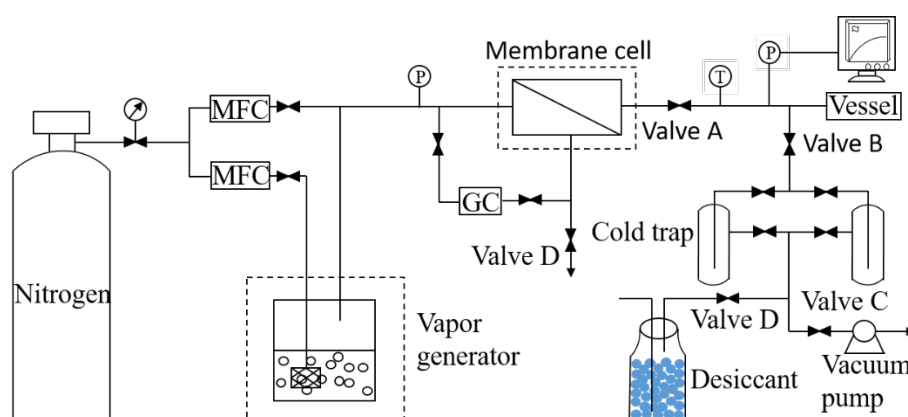


Fig. 1. Schematic diagram of the experimental setup for gas/vapor separation.

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:

$$J = \frac{W}{At} \quad (1)$$

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:

$$P = \frac{JL}{(X_{feed}P_{feed} - X_{perm}P_{perm})} \quad (2)$$

where P_{feed} and P_{perm} are the feed and permeate pressures, respectively, L is the thickness of the PDMS layer, and X_{feed} and X_{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]:

$$P_i = \frac{L273Vdp_i}{A(X_{feed}P_{feed} - X_{perm}P_{perm})T76dt} \quad (3)$$

where L is the thickness of the PDMS layer, X_{feed} and X_{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 [20-22].

Selectivity(α) is calculated as follows:

$$\alpha = \frac{P_{VOC}}{P_{N_2}} \quad (4)$$

where P_{VOC} are permeability of VOC, P_{N_2} are permeability of 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 [23, 24]. During the actual experiments, the membrane selectivity varied with the permeate pressure, and a regression equation ($y = Aexp^{Bx}$) 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 [25]. The simulated conditions were controlled as follows: feed flow rate $100 \text{ Nm}^3 \cdot \text{h}^{-1}$, temperature $30 \text{ }^\circ\text{C}$, feed pressure 0 kPa , and feed concentration $1 \text{ mol}\%$. 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 [25, 26]:

$$P_S = \frac{k}{k-1} q_{V,in} p_{in} \left[\left(\frac{p_{out}}{p_{in}} \right)^{\frac{k-1}{k}} - 1 \right] \quad (5)$$

where k is the isentropic exponent, P_S is the isentropic power, $q_{V,in}$ represents the volume of vapor in the vacuum pump, and p_{in} and p_{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 $30 \text{ }^\circ\text{C}$. This is generally regarded as an ordinary heat exchange process and can be expressed in terms of the energy balance formula.

$$F_{vapor} \Delta H_{vapor} + Q_{pump} - F_{coolant} \Delta H_{coolant} = 0 \quad (6)$$

$$\Delta H = c_p (T_{out} - T_{in}) \quad (7)$$

where F is the inlet flow rate of the pump, ΔH is the enthalpy change of the stream, subscripts *vapor* and *coolant* denote cooled substance and coolant, in order, Q_{pump} is the heat of the pump,

c_p is the heat capacity, T_{in} and T_{out} are the inlet and outlet stream temperatures, respectively.

In the condensation process, the VOC-rich permeate was condensed at $-30\text{ }^\circ\text{C}$ for recovery. Since the condensation process involves phase change enthalpy, the energy consumption is calculated using the following equation:

$$F'_{vapor}\Delta H'_{vapor} + F_{liquid}\gamma_{liquid} - F_{coolant}\Delta H_{coolant} = 0 \quad (8)$$

where F'_{vapor} is the flow rate of the outlet gas of the condenser, $\Delta H'_{vapor}$ is the enthalpy change of non-condensable gas, F_{liquid} is the VOC flow rate of the condenser, and γ_{liquid} is the latent heat of vaporization of VOCs.

3. Results and discussion

3.1 Effect of membrane thickness

In gas separation, 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, shown 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 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 thickness, because the morphology of structure of the synthesized membranes (amorphous in this case) was not significantly affected by the thickness, as previously reported [17]. Furthermore, other reports [22, 24] showed that the impact of free volume changes on permeability of amorphous membranes was much higher compared to crystalline ones. Shishatskii et al.[27] reported the decrease in fractional free volume of the membrane with the decreasing of its thickness. Our results, shown in Fig. 3, demonstrate a higher density for thinner membranes, which typically translates into a lower free

volume [28]. This means that fewer channels and adsorption sites would be available for the diffusion of cyclohexane and nitrogen through the membrane, thereby lowering their permeability.

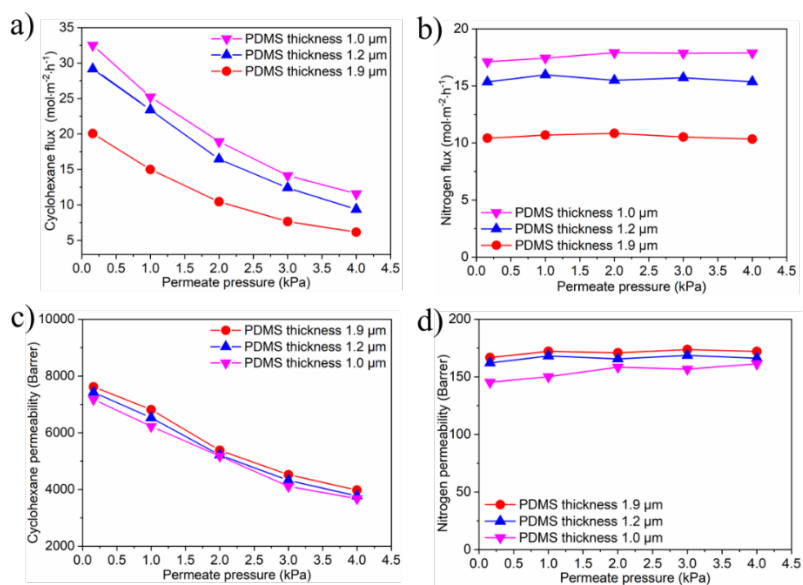


Fig. 2. Flux (a,b) and permeability (c,d) of cyclohexane and nitrogen in the separation of cyclohexane /nitrogen mixtures through polydimethylsiloxane (PDMS) composite membranes of varying thickness versus permeate pressure [feed cyclohexane concentration is 4%, feed pressure is 0 kPa (feed gauge pressure) at 30 °C, and flow rate is 3 L·min⁻¹].

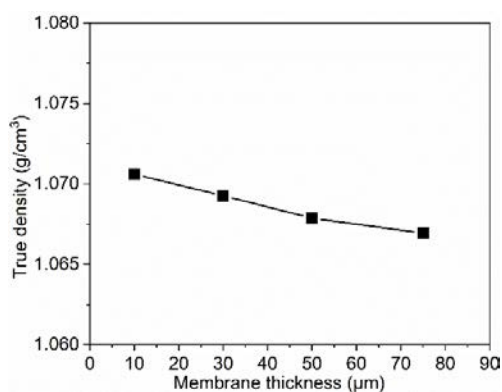


Fig. 3 Density of homogeneous PDMS membrane with different thicknesses

Fig. 2(a) shows that as the permeate pressure increases the cyclohexane flux decreases, and

this is attribute 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 more space is available for nitrogen diffusion. These two opposites behaviors compensate each other, leading to almost constant nitrogen flux (Figs. 2(b)). These results also show that the sensitization of the separated species with high saturated vapor pressure is lower compared to species with low saturated vapor pressure [29]. Fig. 2(c) shows that the cyclohexane permeability decreases almost linearly with increasing permeate pressure, this is attributed to the reduced driving force. The lower permeability of cyclohexane implies a lower cyclohexane transport through the membrane and, consequently, the possibility of higher nitrogen transportation, which results in a slightly higher nitrogen permeability, as shown in Fig. 2(d).

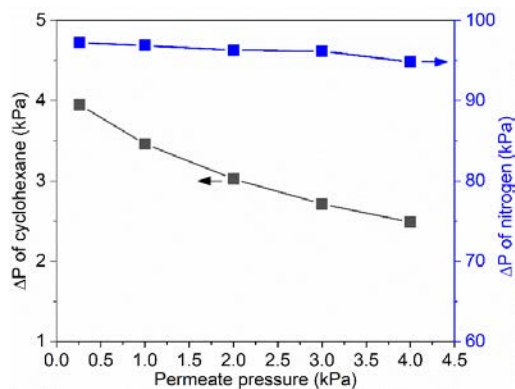


Fig. 4 Relationship between the difference in partial pressures of cyclohexane and nitrogen and permeate pressure

Fig. 5 shows that the selectivity decreases with increasing permeate pressure, this is due to

the simultaneous reduction of the cyclohexane permeability and the slightly increase of the nitrogen one. The morphology of the membrane used in this study is homogeneous [17], so the selectivity should be independent from the thickness [30]. Although the nitrogen permeability improves slightly with the membrane thickness, its value is still one order of magnitude lower than the cyclohexane one. Accordingly, the selectivity seems still being independent from the thickness. Our final conclusion, as possible to evaluate from Figures 2 and 5, is that the increase of the permeate pressure does not lead to the 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.

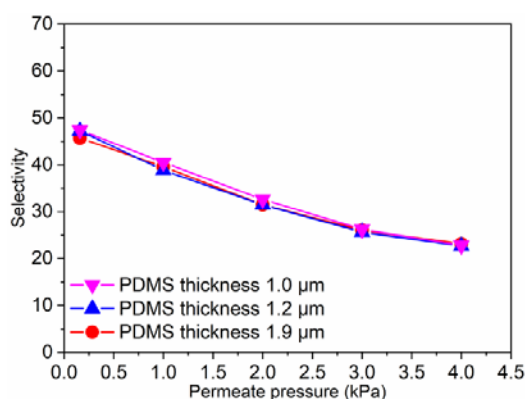


Fig. 5 Cyclohexane /nitrogen selectivity versus permeate pressure

The partial pressure difference (ΔP) of the separated species is the main factor that produces the transmembrane driving force, which induces the transport of the separated species. The membrane is resistant to the transportation of gases, and this resistance is proportional to its thickness. Therefore, a minimum ΔP 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 thicknesses at different ΔP values (which can be obtained by

changing the permeate pressure) was herein studied, as shown in Fig. 6(a). We observed a linear relationship between the cyclohexane flux and ΔP , 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 ΔP can be obtained. This can also be related to the membrane thickness, because the permeation resistance improves with its increase [31]. A higher thickness leads to a higher ΔP , specifically, from 1.71 kPa for a 1 μm thick membrane, to 2.03 kPa, for a 1.9 μm thick one. Fig. 6(b) shows the relationship between the nitrogen flux and ΔP ; a similar trend can be observed: the higher the ΔP the lower the flux. However, the minimum ΔP produced for the nitrogen transportation is much higher compared to the one of cyclohexane. These results suggest that the PDMS membrane is dense and without defects. The low affinity between nitrogen and PDMS is also responsible for the limited adsorption and diffusion of nitrogen through the membrane. This is attributable to the PDMS membrane following a solution-diffusion mechanism for gas/vapor separation that, typically, translates into a high selectivity for the separation of VOCs from nitrogen.

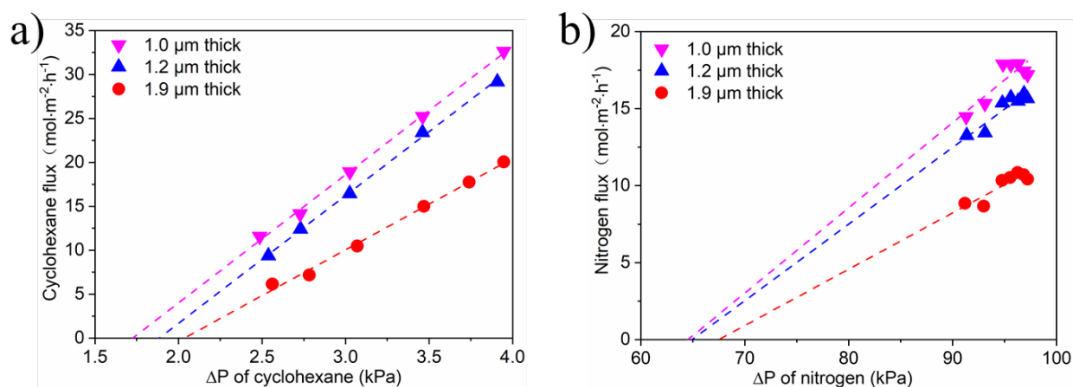


Fig. 6 Relationship between the flux of cyclohexane (a) and nitrogen (b) and the difference in partial pressures created by changing permeate pressure

[feed VOC concentration is 4%, feed pressure is 0 kPa (feed gauge pressure) at 30°C, and flow

rate is 3 L·min⁻¹].

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 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 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 that the VOC properties have on the 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

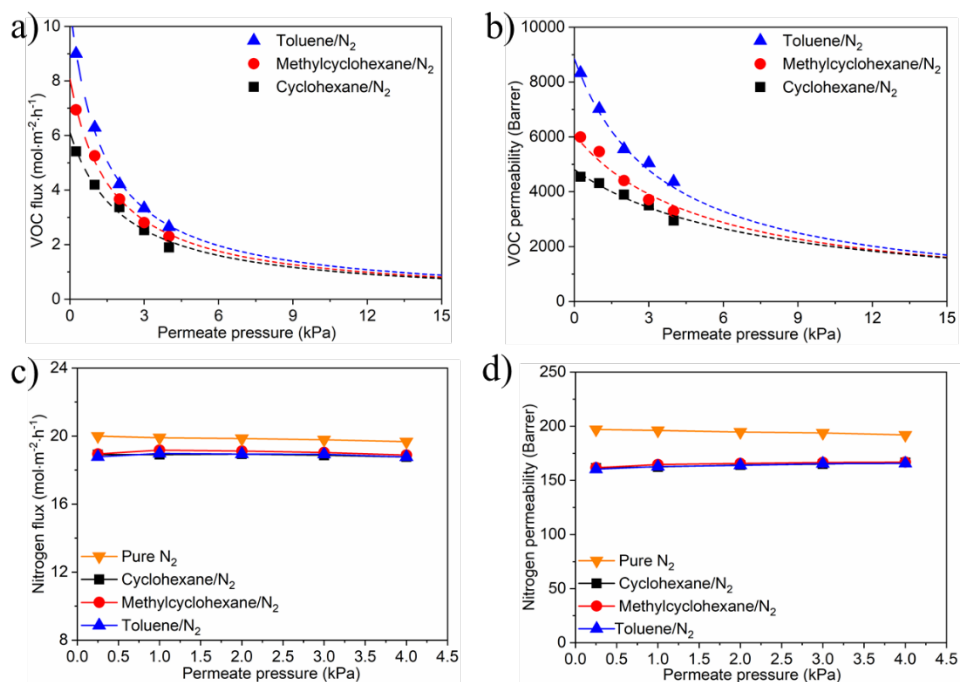


Fig. 7 Flux (a,c) and permeability (b,d) of volatile organic compounds (VOCs) and nitrogen in the separation of VOC/nitrogen mixtures with different saturated vapor pressures

[feed VOC concentration is 1%, feed pressure is 0 kPa (feed gauge pressure) at 30°C, and flow rate is 3 L·min⁻¹].

Table 1 Properties of different VOC compounds

Compound	Formula	Solubility parameter (Mpa ^{1/2})	Molecular weight (g·mol ⁻¹)	Kinetic diameter(Å)	Saturated vapor pressure (kPa)
Toluene	C ₇ H ₈	18.2	92.14	5.85 ^[32]	4.89
Methylcyclohexane	C ₇ H ₁₄	15.9	98.19	6.0 ^[33]	5.33
Cyclohexane	C ₆ H ₁₂	16.7	84.16	6.0 ^[32]	16.2
PDMS		14.9			

VOC: volatile organic compound; PDMS: polydimethylsiloxane.

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 occupying the delivery channels. The kinetic diameter of VOC is large and its diffusion rate is low; this further hampers the permeation of nitrogen [9], thus, a lower nitrogen flux and permeability is observed during its separation from VOC in mixtures, especially compared to the pure nitrogen permeation. Fig. 7(c) and (d) also show that with increasing permeate pressure, the pure nitrogen permeation decreases 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 during the separation from cyclohexane in mixtures, is also consistent with the results shown in Fig. 2(b) and (d).

From Fig. 7, it can also be 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 [34]. 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.

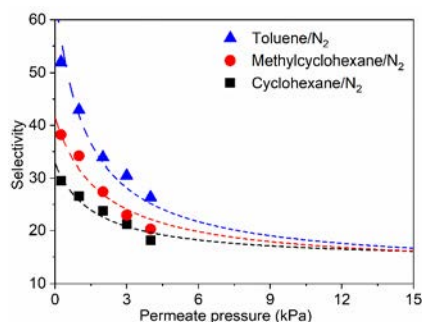


Fig. 8 Relationship between selectivity and permeate pressure in the separation of volatile organic compound (VOC)/nitrogen mixtures with different saturated vapor pressure

[feed VOC concentration is 1%, feed pressure is 0 kPa (feed gauge pressure) at 30°C, and flow rate is 3 L·min⁻¹].

Fig. 9 shows the effects of partial pressure difference (ΔP) and condensability on VOC flux. The results show that, to an increase of partial pressure difference corresponded a boost of 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. This translates into a high flux as, 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 diffusion of VOC through the membrane.

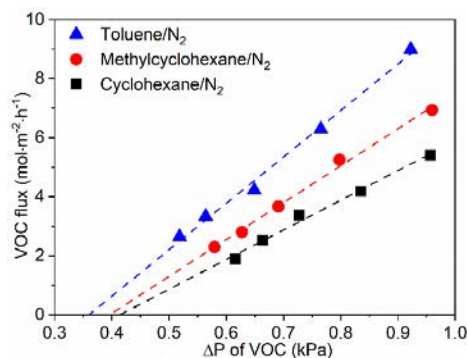


Fig. 9 Flux of volatile organic compound (VOC) in the separation of VOC/N₂ mixtures under different partial pressure difference

[feed VOC concentration is 1%, feed pressure is 0 kPa (feed gauge pressure) at 30°C, and flow rate is 3 L·min⁻¹].

3. 3 Effect of feed cyclohexane concentration

Fig. 10 displays the flux and the permeability of cyclohexane and nitrogen, regarding the separation of their mixtures at different feed cyclohexane concentrations and permeate pressures. From Fig. 10(a) is evident, that a high feed concentration of cyclohexane indicates a high probability for its molecules to come in contact and get adsorbed into the membrane, which leads 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 in the membrane. These results also, indirectly, explains the long-term stability of the membrane, as shown in Fig. 11. In fact, during the 300 days measurement, the PDMS selective layer tightly anchors to the substrate because of the negligible swelling. If the latter is strong, instead, the frequent switching of vacuum pump under experimental conditions is known to lead to the peel-off of the PDMS selective layer from the substrate and, eventually, to the breaking of the membrane.

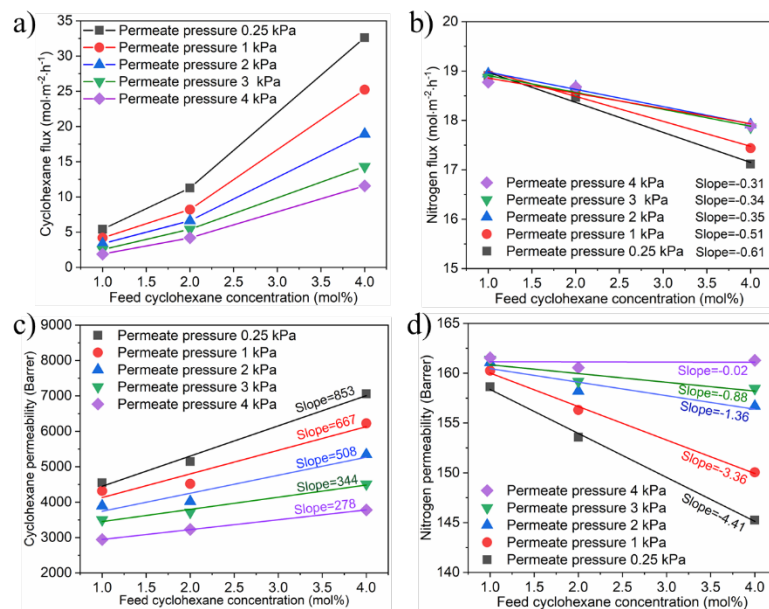


Fig. 10 Flux (a, b) and permeability (c, d) of cyclohexane and nitrogen in the separation of cyclohexane /nitrogen mixtures by polydimethylsiloxane (PDMS) composite membrane versus permeate pressure at different feed cyclohexane concentrations [membrane thickness is 1 μm ,

feed pressure is 0 kPa (feed gauge pressure) at 30°C, and flow rate is 3 L·min⁻¹].

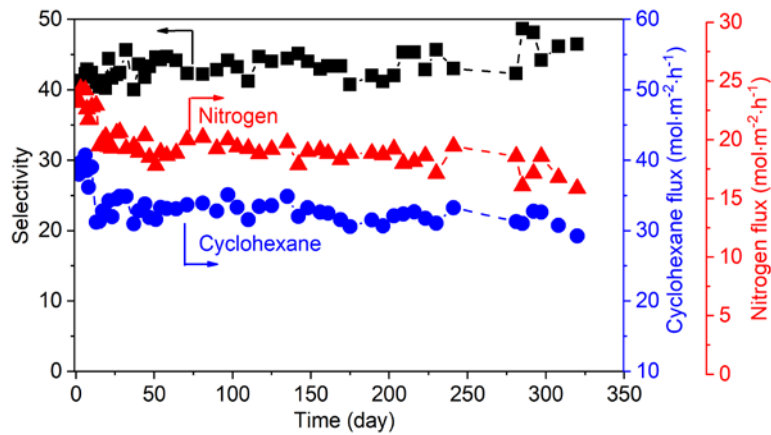


Fig. 11 Stability of PDMS composite membrane in the separation of cyclohexane/nitrogen mixture [feed cyclohexane concentration is 1 %; feed pressure (feed gauge pressure) and permeate pressure is 0 kPa and 5000 Pa, respectively, at 30°C; and flow rate is 3 L·min⁻¹].

With decreasing permeate pressure, a higher driving force is produced on both sides of the membrane so that more cyclohexane molecules can be adsorbed. The latter, forces the membrane to swell improving the cyclohexane flux and, gradually, the feed cyclohexane concentration starts deviating from linearity. 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.

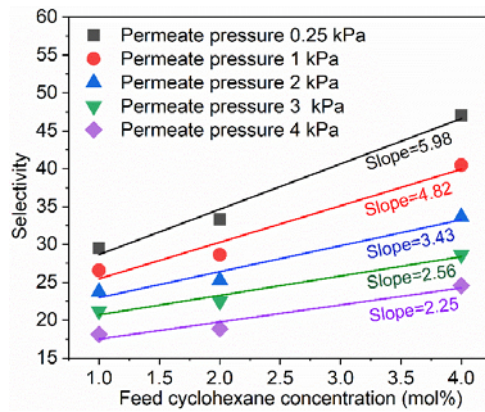


Fig. 12 Relationship between feed cyclohexane concentration and selectivity

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 as, because of its higher vapor concentration, it is more likely to be condensed in the pores or on the membrane surface via capillary condensation [35, 36]. Lue et al.[37] 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 [36]. This also results in a higher minimum partial pressure difference (ΔP) in the diffusion of cyclohexane at higher feed cyclohexane concentrations. Additionally, these results also indicate that under the same separation conditions (partial pressure difference and adsorbed amount on the membrane surface), the flux of gas/vapor separation can be higher than that of pervaporation, owing to the higher diffusion coefficient in the former.

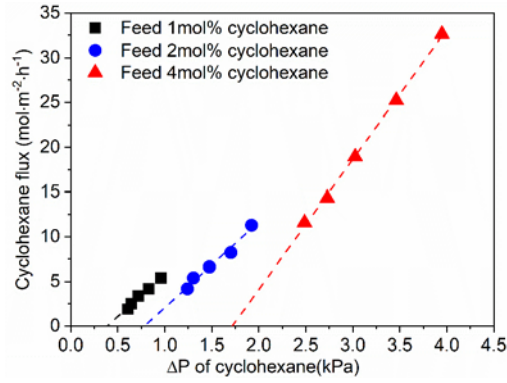


Fig. 13 Relationship between cyclohexane flux and the difference in partial pressure created by changing the permeate pressure for cyclohexane/N₂ mixture separation

[feed pressure is 0 kPa (feed gauge pressure) at 30°C and flow rate is 3 L·min⁻¹].

3. 4 Effect of feed temperature

Besides pressure, permeability is also a function of temperature [17, 34], which can be described using the Arrhenius equation:

$$p = p_0 \exp\left(-\frac{E + \Delta H}{RT}\right) \quad (9)$$

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 $E + \Delta H$ (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 diffusion through the membrane, given that the diffusion activation energy is usually positive, whereas the heat of the solution is negative, in agreement with previously reported studies [34]. 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 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 diffusion (as already discussed), eventually leading to a lower diffusion coefficient at a higher permeate pressure.

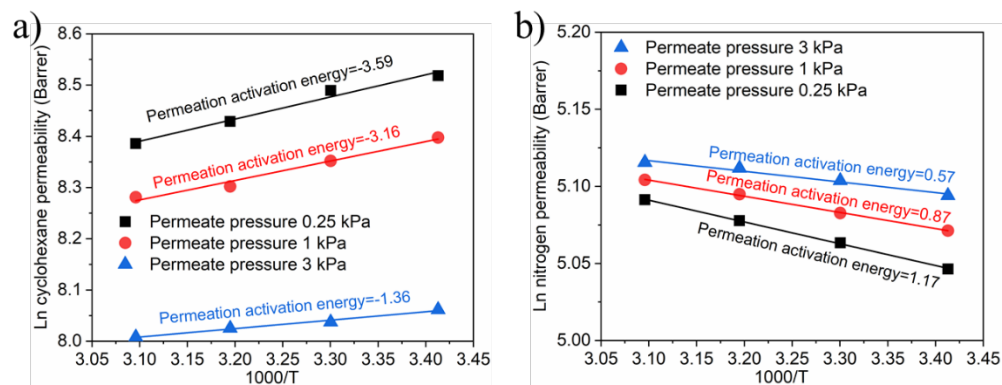


Fig. 14 Arrhenius plots of cyclohexane permeability (a) and nitrogen permeability (b) at different reciprocal temperatures in the separation of cyclohexane /nitrogen mixtures by PDMS composite

membrane versus permeate pressure at different temperatures

[membrane thickness is 1 μm , feed pressure is 0 kPa (feed gauge pressure), feed cyclohexane

concentration is 2 mol%, and flow rate is 3 $\text{L}\cdot\text{min}^{-1}$].

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 [38]. Conversely, for nitrogen the diffusion step is the dominating factor, and this is due to its lower affinity for the PDMS membrane. 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 high cyclohexane flux, but a low 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).

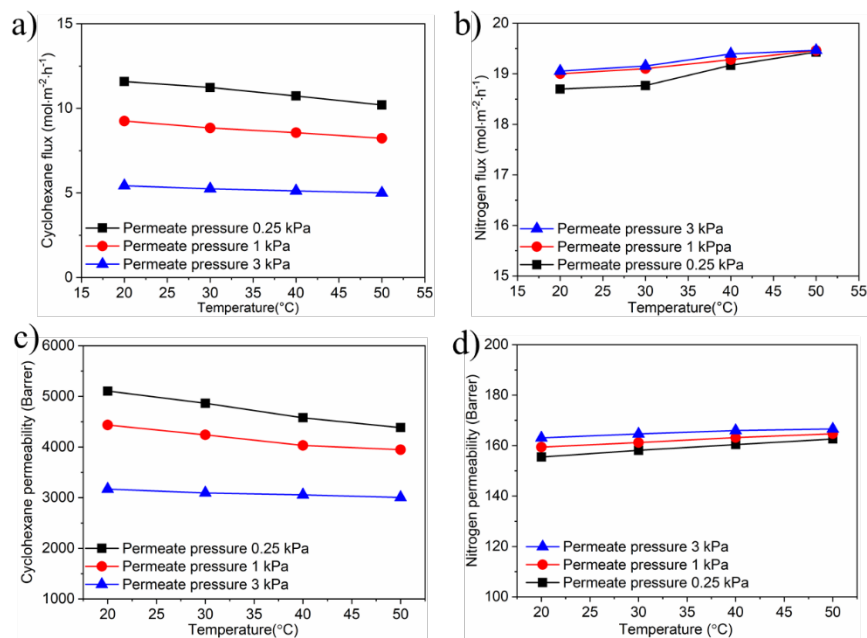


Fig. 15 Flux (a, b) and permeability (c, d) of cyclohexane and nitrogen in the separation of cyclohexane /nitrogen mixtures by polydimethylsiloxane (PDMS) composite membrane versus

permeate pressure at different temperatures

[membrane thickness is 1 μm , feed pressure is 0 kPa (feed gauge pressure), feed cyclohexane concentration is 2 mol%, and flow rate is 3 L·min⁻¹].

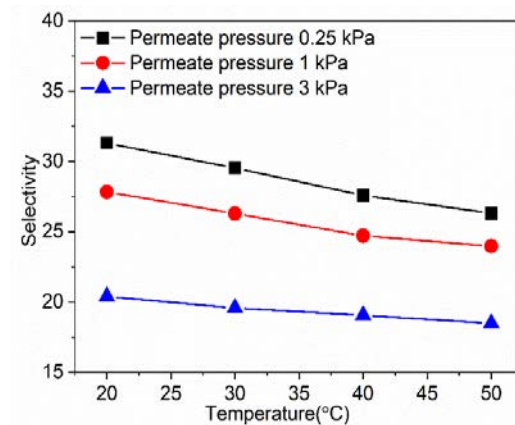


Fig. 16 Selectivity in the separation of cyclohexane /nitrogen mixtures by polydimethylsiloxane (PDMS) composite membrane versus permeate pressure at different temperatures

[membrane thickness is 1 μm , feed pressure is 0 kPa (feed gauge pressure), feed cyclohexane concentration is 2 mol%, and flow rate is 3 L·min⁻¹].

3. 5 Variation in energy consumption with permeate pressure

As thoroughly discussed, a high permeate pressure results in low separation performance, since the sensitization 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 separation of VOC at low saturated vapor

pressure needs more energy compared to high saturated one, due to the more difficult condensability of the former. Both low and high permeate pressures do not lead to a decrease in the energy consumption if a dry vacuum pump is used. This happens 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 [39]. Furthermore, the compression process generates heat and cooling is necessary to avoid overheating, which also leads to a higher energy consumption. Therefore, we can say that the lower the permeate pressure, the higher the energy consumptions, and this is valid for 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 under high pressure. Because of that, a larger volume of gas 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.

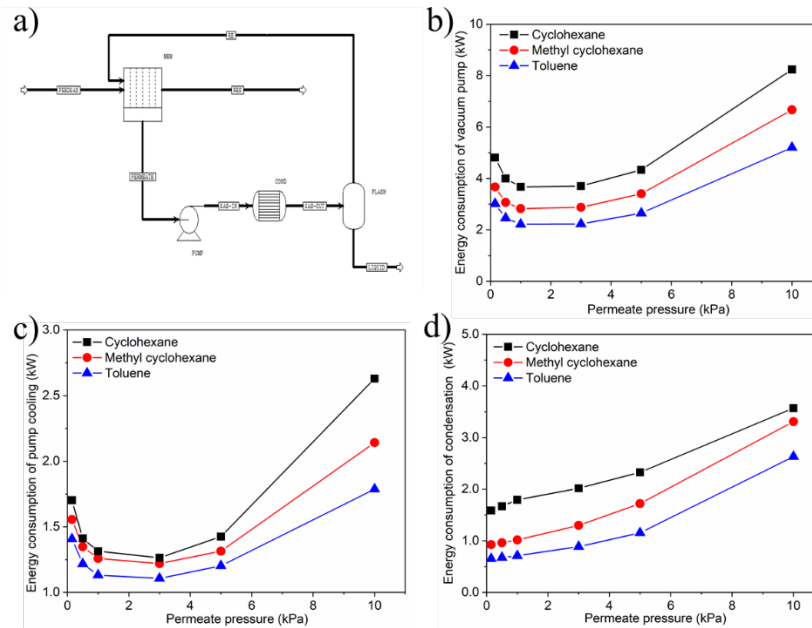


Fig. 17 Energy consumption simulation of membrane/condensation technology under different permeate pressures (a: flow chart: condensation after vacuum pump; b: energy consumption of vacuum pump; c: energy consumption of pump cooling; d: energy consumption of condensation)

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 sensitization of the separated species with a high saturated vapor pressure resulted lower than the correspondent at 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 hampers 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.

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