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Symposium documents for

Lui Li

Abstract

Presentation

VOCs separation from N_2 by poly(ether block amide) membranes

Li Liu, Xianshe Feng and Amit Chakma
(Dept. of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1)

Introduction

The vent streams from many manufacturing processes in chemical, petrochemical and pharmaceutical industries, fuel storage and painting operations often contain a large amount of volatile organic compounds (VOCs). Separation processes are needed to recover the VOCs and minimize their emissions into air. Most traditional methods, such as adsorption and low temperature condensation, have so far been found to be unsatisfactory. It has been shown that membrane processes are favorable over other processes for relatively small feed gas flow rates when the VOC concentrations in the vent streams are not too low.

Membrane based gas or vapor separation is a pressure driven process, and the membrane selectivity determines the recovery (i.e. process efficiency) directly. For VOCs separations, membranes are required to have a much higher permeability to VOCs than to nitrogen or air. In this work, rubbery poly(ether block amide) (PEBA) (type 2533) membranes were studied for VOCs separation from N_2. PEBA has micro-biphasic structure; the rubbery polyether segments offer high permeability to organic vapors, while the glassy polyamide domain restricts membrane swelling. Therefore, it is expected that PEBA membranes will yield a better permselectivity than silicone rubber-based membranes, which are the representative membranes for this application. The organic vapors studied include pentane, hexane, cyclohexane, heptane, methanol, ethanol, n-propanol, n-butanol, acetone, dimethyl carbonate (DMC) and methyl *tert*-butyl ether (MTBE).

Experimental

Ultra-thin PEBA membranes were prepared by the liquid surface spreading method developed recently in our lab. The ultrathin PEBA layer was laminated on porous polysulfone substrates to form a thin film composite membrane. This structure was found to have less resistance from the substrate for fast VOCs permeation than the traditional composite membrane prepared by the dip coating method.

Figure 1 is the experimental set-up for VOCs/N_2 separation. During the experiments, the feed mixture was kept at atmospheric pressure, and vacuum (< 1 kPa abs.) was applied to the permeate side. The VOC concentration in the feed stream was controlled by adjusting the pressure of the solvent bubbling tank. The VOCs permeated through the membranes were collected in a cold trap to determine the permeation rate. The flow rates and concentrations of the feed and permeate streams were measured, and the membrane performance is characterized in terms of permeance (defined as the permeation flux normalized by the partial pressure difference across the membrane) and selectivity (i.e. the permeance ratio of VOCs over nitrogen).

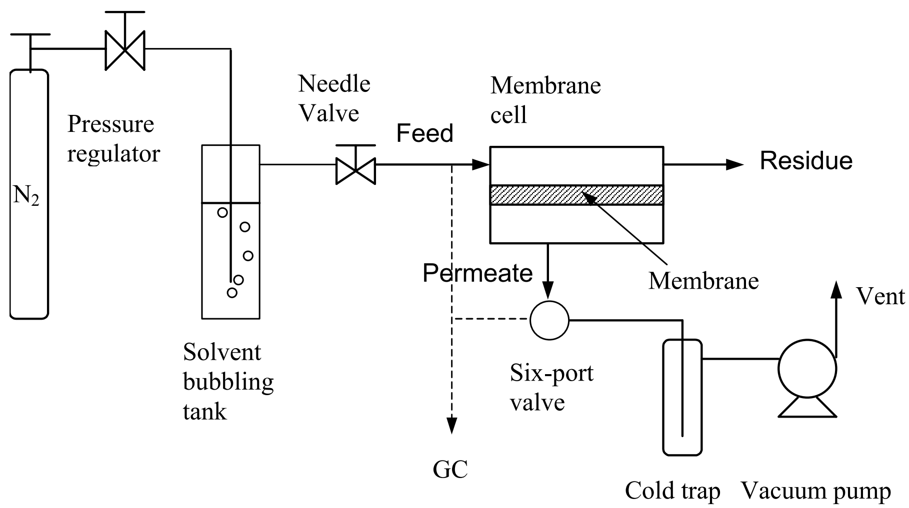

Fig.1 Schematic diagram of VOCs/N_2 separation system

A very low stage cut was used in the experiments to maintain constant concentration of VOCs along membrane surface at the feed side so that the membrane performance at a given feed concentration can be evaluated. The feed flow rate was as high as 400 cm^3 (STP)/min to reduce the effect of the boundary layer.

Results and discussion

The permeation of VOCs/N_2 through the membranes at different feed concentrations was investigated. The membranes had much higher permeability to VOCs than to nitrogen. At a given feed concentration, the permeance of the four paraffin compounds tested follows the order of heptane > cyclohexane > hexane > pentane. For the other VOCs, the magnitude of the permeance is n-butanol > n-propanol > DMC > ethanol > methanol > acetone > MTBE. Generally, gas permeation through rubbery membranes is controlled by sorption. The sorption behavior, mainly determined by the condensability of the permeant, contributes significantly to the selective permeation. Therefore, for the paraffin and the alcohol compounds, condensable vapors tend to have high permeabilities.

Figure 2 shows the permeance of the four paraffin vapors as a function of feed pressure. Because of membrane swelling caused by the organic vapor molecules, the permeance of VOCs increase with an increase in the feed VOC concentration. As VOC condensability increases the concentration dependency of VOC permeance becomes significant. The permeation of other VOCs exhibits similar behavior. The permeance of N_2 also increases with an increase in feed VOC concentration, which is mainly attributed to the membrane swelling at high feed concentrations. Furthermore, for different VOC/N_2 mixtures, the N_2 permeance tends to be higher when a high permeability VOC is present, indicating that the permeance of N_2 is significantly affected by the presence of VOC. Moreover, the VOC/N_2 selectivity increases with an increase in feed VOC concentration. This shows that increasing VOC concentration will increase the VOC permeance more significantly than the N_2 permeance. Therefore, the membrane is more selective at higher VOC concentrations. A selectivity of 40 to 180 was obtained for paraffin/N_2 separation, which are higher than the selectivities reported for silicone rubber membranes. At a given feed concentration, alcohol compounds were found to have higher VOC permeance and selectivity than hydrocarbon vapors, presumably due to the stronger affinity of polar alcohol molecules with the polyether linkage. That PEBA 2533 can be dissolved in propanol and butanol demonstrates the high affinity of the solvents and the polymer. Table 1 shows the permeance and selectivity of VOCs/N_2 at 23 ^oC when the feed gas is 80 % saturated with the organic compounds. The effect of temperature on membrane permeability was investigated, and the permeance of both VOC and N_2 was found to follow the Arrhenius type relation.

As shown in Figure 3, the permeate concentration was found to increase significantly with an increase in the feed VOC concentration. Generally, when the feed VOC concentration is over 5%, a permeate VOC concentration of 90 mol% can be achieved readily. This also demonstrates that the membrane is efficient for the separation of VOCs from N_2 at relatively high feed VOC concentrations.

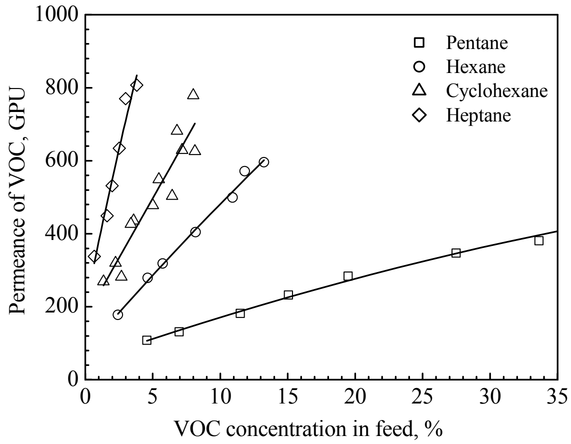

Fig 2. Permeance of VOC as a function of feed concentration

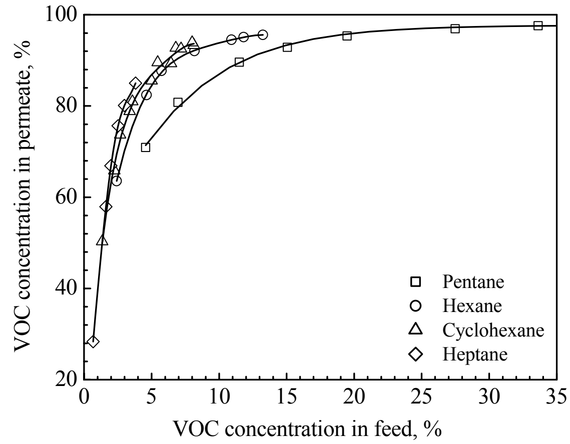

Fig 3. VOC concentration in permeate as a function of feed concentration

The effect of membrane thickness on the separation performance was studied by using two membranes with different thickness of the PEBA layer. The thinner membrane showed a lower selectivity than the thicker one, especially at high feed concentrations, though the thinner had a higher VOC permeance. This can be attributed to the boundary layer effect or the resistance of the substrate layer due to the high permeation rate of VOC. Therefore, the optimization of the flow pattern and the membrane structure are important in order to maximize the membrane performance.

Table 1 Permeance and selectivity of VOCs/N_2 at 23 ^oC (the feed 80% saturated with VOCs)

Mixtures	Permeance, GPU		Selectivity of
	VOC	N_2	VOC/N_2
Pentane/N_2	380.7	4.76	80
Hexane/N_2	596.1	4.21	142
Cyclohexane/N_2	626.3	3.97	158
Heptane/N_2	807.0	5.64	143
Methanol/N_2	1178.3	3.77	313
Ethanol/N_2	913.8	4.23	216
n-Propanol/N_2	551.9	4.41	125
n-Butanol/N_2	389.4	5.63	69
Acetone/N_2	929.4	4.99	186
DMC	1186.0	7.23	164
MTBE	602.5	6.21	97

At a given feed concentration, the separation performance at different stage cuts was also studied for hexane/N_2 mixture. At a feed concentration of 12 mol%, more than 90 % hexane could be recovered at a stage cut of 0.16, for which the permeate hexane is about 70 mol%. Therefore, the PEBA/polysulfone composite membranes could be used to recover gasoline vapors efficiently to control the emission of gasoline vapors into the air.

Conclusions

The separation of VOC/N_2 mixtures by PEBA 2533 composite membranes were studied; it is relevant to the recovery and separation of gasoline vapor and other organic vapors from air. The membranes show good permselectivity for VOC/N_2 separation. The permeance of VOC and N_2 increases with an increase in the feed VOC concentration. The permeance of N_2 is affected by the presence of VOC significantly. Generally, more than 90 mol% VOC in permeate can be achieved when the feed concentration of VOC is over than 5 mol%. Because of the high permeability of the VOCs in the membranes, the resistance of the support layer and boundary layer effect were found to be significant. Further studies on optimizing the membrane structure and minimizing the boundary layer effect are needed to improve the separation performance of the membrane.

VOCs/N_2 separation by poly(ether block amide) composite membranes

L. Liu, X. Feng and A. Chakma

Department of Chemical Engineering
University of Waterloo
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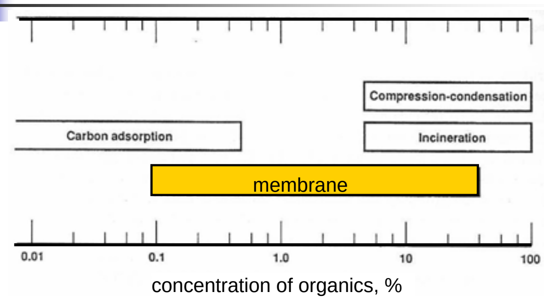
Outline

- Introduction
- Experimental
  - Membrane preparation
  - Separation process
- Results and discussion
  - VOCs/N_2 separation
  - Resistance of support layer
- Conclusions

Introduction

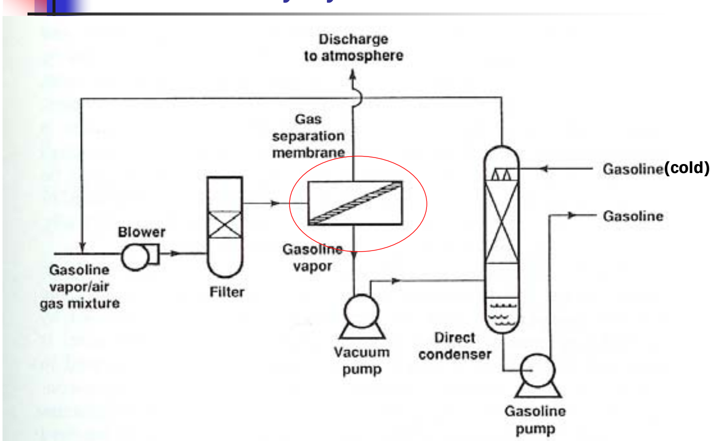
- Many industrial processes release Air/N_2 streams containing volatile organic compounds (VOCs)
  - Petrochemical & chemical industries
  - fuel storage, loading & unloading
  - coating & painting operations
  - Environmental problem
  - Economic loss

VOCs treatment technology



- Membrane separation
  - Energy efficient
  - Reuse of recovered solvents

VOC recovery by membrane

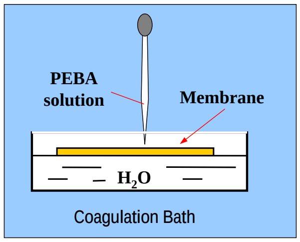


Membrane material

- Rubbery polymer: high solubility for VOCs
  - Silicone rubber: selectivity 10-100
- Poly(ether block amide) (PEBA) 2533
  - An alternative rubbery polymer to silicone rubber
  - Copolymer
    - 20 wt% polyamide: mechanical strength, chemical resistance
    - 80 wt% polyether: high chain mobility, high free volume
  - Good membrane formation characteristics
  - Good permeation performance
    - CO_2/N_2 separation, pervaporation

Membrane preparation

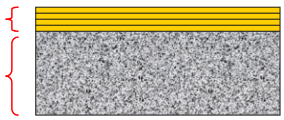
Thin skin membrane: water surface spreading



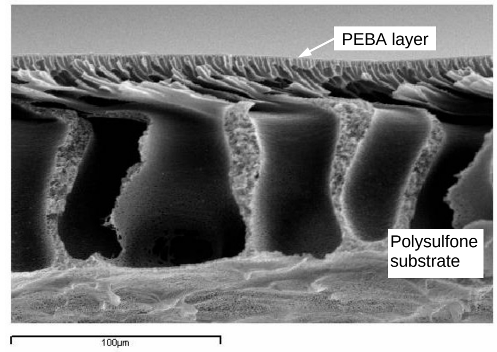
L. Liu, A. Chakma, X. Feng, J. Membr. Sci., 235 (2004) 43-52

Composite membrane:

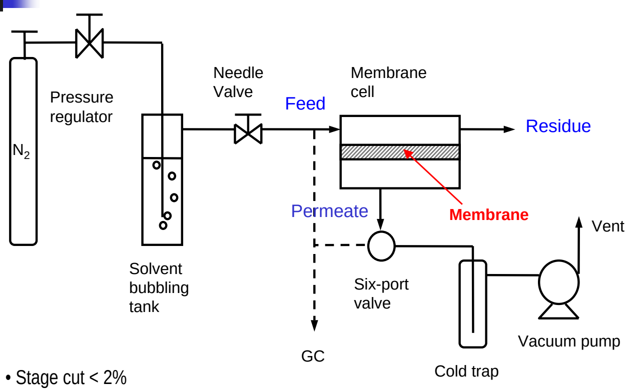
Multi-layer lamination



PEBA/polysulfone composite membrane



VOCs separation set-up



- Stage cut < 2%
- @ room temp.

Permselectivity

- Permeance $$J_i = \frac{Q \cdot y_i}{A.(p_h \cdot x_i - p_l \cdot y_i)}$$
- Selectivity $$\alpha_{i/j} \equiv \frac{y_i / y_j}{x_i / x_j} = \frac{J_i}{J_j}$$

J : permeance, GPU (1 GPU= 10^{-6} cm^3(STP)/cm^2.s.cmHg)

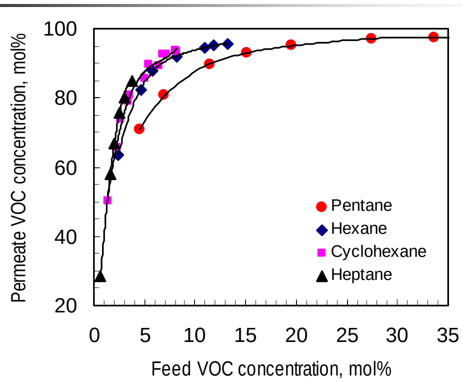
Q: permeate flow rate, cm^3(STP)/s

x_i, y_i: mol frac of VOC in feed & permeate

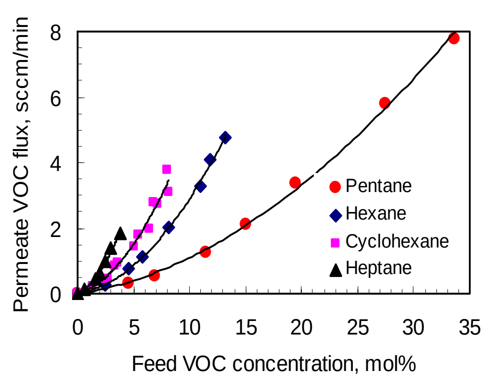
p_h, p_l: pressure in feed & permeate, cmHg

A: effective membrane area, cm^2

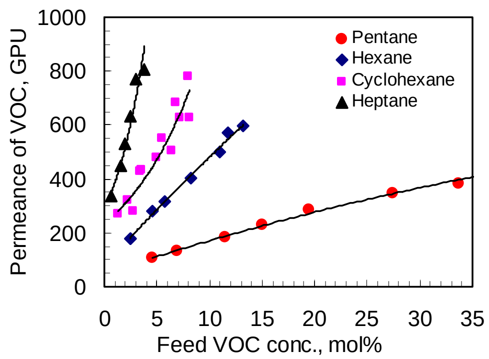
VOC separation from nitrogen



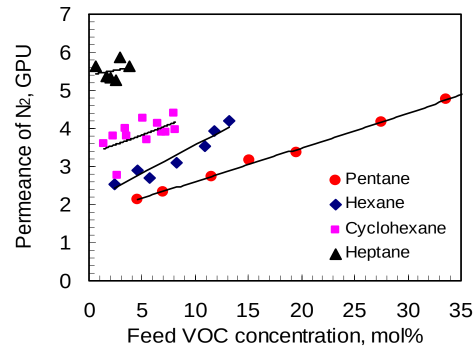
VOC concentration in permeate



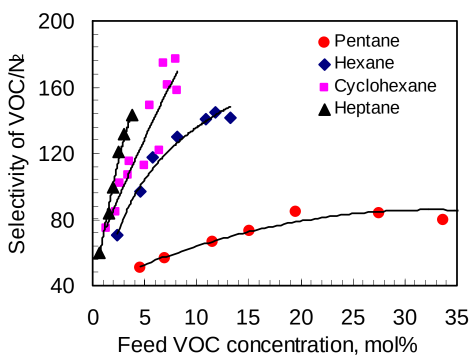
Permeation flux of VOC



Permeance of VOC vs. feed VOC concentration



Permeance of N_2 vs. feed VOC concentration



Selectivity of VOC/N_2 vs. feed VOC concentration

Permeance of VOCs

- Hydrocarbons (main components of gasoline)
  heptane > cyclohexane > hexane > propane
- Others
  n-butanol > n-propanol > dimethyl carbonate > ethanol > methanol > acetone > methyl tert butyl ether
- alcohol > hydrocarbon

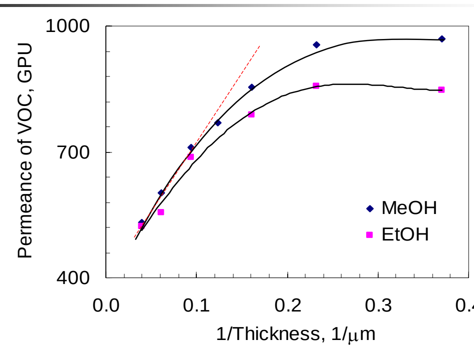
- condensiblity → solubility → permeability
- interaction

VOCs/N_2 separation performance (80% feed saturated)

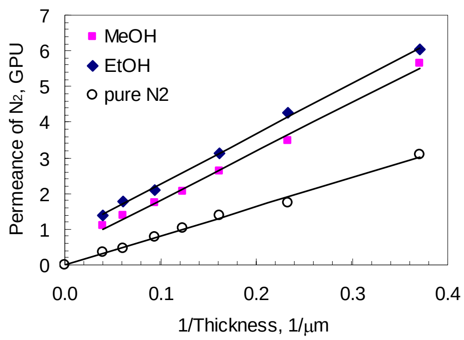
Mixtures	Permeance, GPU		Selectivity VOC/N_2	Silicone rubber Selectivity*
	VOC	N_2		
Pentane/N_2	381	4.76	80	66.8
Hexane/N_2	596	4.21	142	25.7
Cyclohexane/N_2	626	3.97	158	
Heptane/N_2	807	5.64	143	
Methanol/N_2	1180	3.77	313	38.0
Ethanol/N_2	914	4.23	216	
n-Propanol/N_2	552	4.41	125	
n-Butanol/N_2	389	5.63	69	
Acetone/N_2	929	4.99	186	16.1
DMC	1190	7.23	164	
MTBE	603	6.21	97	

* Literature data

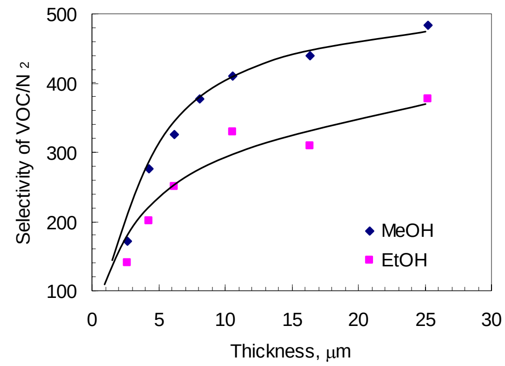
Effect of membrane thickness



VOC permeance vs. reciprocal of PEBA layer thickness
(feed methanol conc. 7.4%, ethanol conc. 3.4%)

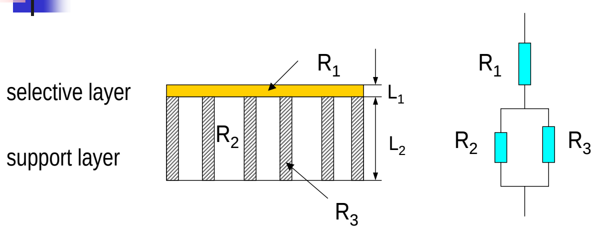


N_2 permeance vs. reciprocal of membrane thickness
(feed methanol conc. 7.4%, ethanol conc. 3.4%)



VOC/N_2 selectivity vs. membrane thickness
(feed methanol conc. 7.4%, ethanol conc. 3.4%)

Resistance of support layer



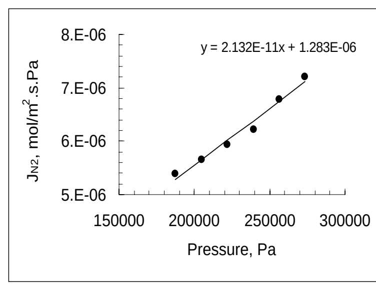
$$R_t = R_1 + \frac{R_2 R_3}{R_2 + R_3} \cong R_1 + R_2 \quad (R_2 << R_3) \qquad J = \frac{1}{R_t A}$$

$$R_1 = \frac{L_1}{P_1 A} = \frac{1}{J_1 A} \qquad R_2 = \frac{L_2}{A\varepsilon}\left(\frac{9\pi MRT}{32}\right)^{1/2}$$ (Knudsen flow)

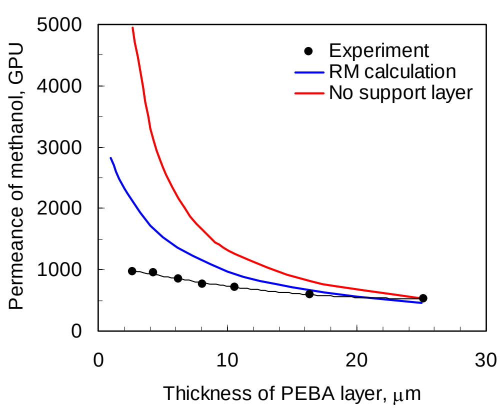
Structural parameter of substrate

- Gas permeation method: $J = \frac{\varepsilon r^2}{8\eta RTL_2}\bar{p} + \frac{4}{3}\sqrt{\frac{2}{\pi MRT}}\cdot\frac{\varepsilon}{L_2}\cdot r$

Viscous flow — Knudsen flow



$$r = 2.3\times10^{-8} m$$
$$\frac{\varepsilon}{L_2} = 1.4\times10^{4} m^{-1}$$



Effect of membrane thickness on methanol permeance
(feed conc. 7.4%)

Conclusions

- PEBA 2533 membranes exhibited good permselectivity for VOC separation from nitrogen.
- A permeate VOC concentration of 95% can be achieved.
- Both VOC permeance and VOC/N_2 selectivity increased with an increase in the feed VOC concentration.
- The permeation of N_2 was affected by the coupling permeation of VOC due to penetrant interaction & membrane swelling.
- The membrane permselectivity was lowered by the resistance of the porous substrate.

Thank you!