Natural Gas Separation Using Supported Liquid Membranes

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Introduction

The recovery of condensable hydrocarbons ($\geq C_2$) from natural gas by low-temperature condensation or oil absorption provides a major source of hydrocarbon feedstocks for the petrochemical industry. Membrane technology could provide an alternative processing scheme, but conventional polymeric membranes are unsuitable because of low permeabilities (dense films) or poor separation (microporous films). Similarly, the use of carrier-facilitated membranes of the type described by Ward (1972) is not feasible because of the absence of a sufficiently specific carrier. However the use of a supported liquid membrane, in which a liquid hydrocarbon is supported on a microporous substrate and mass transfer occurs by a passive solution and diffusion mechanism, appears attractive. This note reports preliminary studies to determine the performance of such a system.

Experimental

Supported liquid membranes were made by impregnating the chosen microporous support with either *n*-decane or *n*-hexadecane by a soaking procedure. The majority of experiments used Millipore VSWP membrane (pore size 0.025 μm, porosity 70%, cellulosic); others used Millipore type GVHP membrane (pore size 0.22 μm, porosity 75%, PVDF). Tests showed that substantially all of the pore volume was liquid-filled. The treated membrane was placed in a circular permeation cell of flow area 38.5 cm^2, and natural gas at 360 kPa absolute and 20°C was passed through the cell at a rate significantly higher than the permeation rate. A helium sweep on the permeate side was used to adjust the partial pressure gradient, while maintaining the total pressure difference across the membrane below 100 kPa (lower than the bubble point of the membrane).

The concentrations in the permeate were measured by gas chromatography, and those in the retentate were determined by a material balance except at low partial pressure gradients, when they were measured directly. The natural gas used was dry, with a composition in vol. % of: $CH_4 = 90.8$, $C_2H_6 = 4.9$, $C_3H_8 = 1.19$, $iC_4H_{10} = 0.26$, $nC_4H_{10} = 0.15$, $CO_2 = 1.42$, and others (N_2, C_5+, etc.) $= 1.28$.

Theory

Gas transport is assumed to be by a solution diffusion mechanism through the liquid in the pores. It is also assumed for each species that solubility is governed by Henry's law, and that diffusion is independent of concentration and the presence of other species. Bulk flow terms in the diffusion equation are neglected.

With these assumptions the molar flux n_i of each species relative to the membrane surface is:

$$n_i = cD_{iom}(x_{ir} - x_{ip})/t \tag{1}$$

where D_{iom} is related to molecular diffusivity and membrane properties:

$$D_{iom} = D_{io}\epsilon/\tau \tag{2}$$

assuming interfacial equilibrium and using Henry's law:

$$n_i = c\epsilon D_{io}(P_r y_{ir} - P_p y_{ip})/H_{io}\tau t \tag{3}$$

Volumetric flux at standard conditions is $q_i = n_i v_{stp}$, so permeability $\bar{p}_i$ may be defined:

$$\bar{p}_i = q_i/[(P_r y_{ir} - P_p y_{ip})/t] \tag{4}$$

$$= v_{stp}c\epsilon D_{io}/H_{io}\tau \tag{4a}$$

where $\bar{p}_i$ has the units m^3(STP) · m/m^2 · s · kPa.

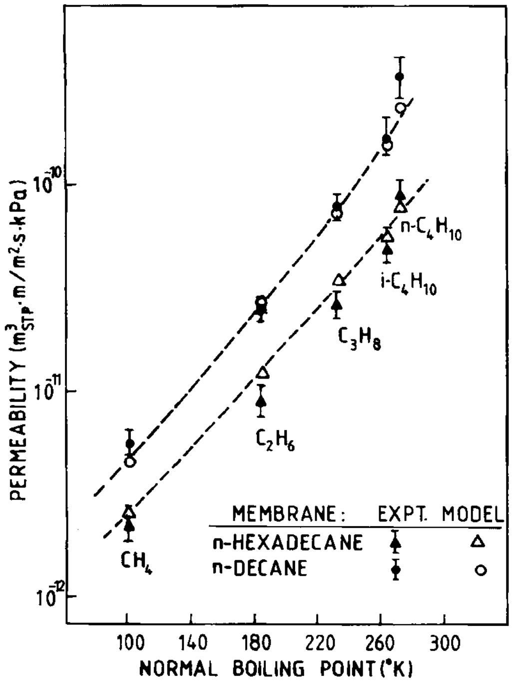

Figure 1. Predicted and average experimental permeabilities.

Separation factors relative to methane are defined by:

$$\alpha_i = \bar{p}_i/\bar{p}_{CH4} \qquad (5)$$

Predictions using Eq. 3, 4, 4a, and 5 have used Henry's law coefficients from the data of Chappelow and Prausnitz (1974), Cukor and Prausnitz (1972), DePriester (1953), Monfort and Arriga (1980), and Wilcock et al. (1978), and diffusion coefficients from the correlation of Hayduck and Minhaus (1982, 1983).

Results

The average experimental permeabilities and those predicted by the simple diffusion model are plotted as a function of the normal boiling point of the permeating species in Figure 1. In calculating the predicted permeability a support porosity of 70% (the same as for the VSWP support) and a support tortuosity of 3.0 (typical of cellulosic films, see Perry and Green [1984] pp. 17–20) were used. This figure shows that the permeability increases with the molecular weight of the permeating species. This is significant because it means that the condensables ($\geq C_2$) were preferentially transferred relative to the major component, methane. Permeabilities were relatively constant over the range of hydrocarbon partial pressure differences tested (approx. 350 to 250 kPa). Values of $\bar{p}_i$ predicted from Eq. 4a are also independent of pressure, and Figure 1 shows that the simple solution diffusion model gives values close to those measured. Errors in the diffusion coefficients and assumed membrane properties could account for the small discrepancies observed.

Table 1 compares the performance of the supported liquid membranes to two types of polymer membranes. The liquid membranes have higher permeabilities and separation factors than the TFE membrane, which also had the disadvantage of preferential transport of methane. Both liquid membranes had significantly higher separation factors than the PDMS membrane, with the permeability of the *n*-decane membrane to condensables being two or three times higher. Table 1 also includes, in parentheses, separation factors predicted from Eqs. 4a and 5, which compare well with the experimental values.

Comparing the two carriers, the *n*-decane performed better in terms of both permeabilities and separation factors. However these advantages may be offset by its greater volatility. There was no detectable difference between the performance of the two microporous supports, however the smaller pore size VSWP support would be more stable since it has a higher bubble point pressure. Future work is aimed at investigating the performance and stability of these membranes at higher pressures.

Conclusions

Supported liquid membranes using hydrocarbon oil carriers are potentially attractive as a means of recovering natural gas condensates. Membrane performance can be readily predicted from solution diffusion data and properties of the porous support.

Acknowledgment

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Notation

c = molar density of liquid, gmol/m^3
D = binary diffusion coefficient, m^2/s

Table 1. Permeabilities and Separation Factors of Light Hydrocarbons through Supported Liquid and Polymer Membranes

	Permeability, $\bar{p}_i$ m^3(STP) · m/m^2 · s · kPa × 10^{11}**				Separation Factor, α_i			
Species	*n*Dec	*n*Hex	PDMS	TFE	*n*Dec	*n*Hex	PDMS	TFE
CH_4	0.58	0.24	0.98	0.0098	1.0(1.0)*	1.0(1.0)*	1.0	1.0
C_2H_6	2.6	0.90	—	0.0060	4.4(5.7)	3.8(4.7)	—	0.6
C_3H_8	8.3	2.7	4.9	0.0030	14.9(15.7)	11.3(12.4)	5.1	0.3
iC_4H_{10}	17.0	5.0	6.1	0.0023	29.9(36)	20.6(20.9)	6.2	0.2
nC_4H_{10}	35.0	9.0	11.0	0.0007	59.7(52.5)	37.5(32.3)	11.5	0.08

Membranes: *n*Dec, *n*-decane; *n*Hex, *n*-hexadecane (this work). PDMS, polydimethylsiloxane/polystyrene copolymer (Barrie and Munday, 1983). TFE, polytetrafluoroethylene/polyfluoroethylene-propylene (Yi-Yan et al., 1980).

*Figures in parentheses are predictions from Eqs. 4a and 5.

**To convert to [cm^3(STP)]cm/cm^2 · s · cmHg, multiply by 1.33 × 10^4.

H_{io} = Henry's law coefficient, kPa
n = molar flux across the membrane, gmol/s · m^2
P = pressure, kPa
$\bar{p}$ = permeability, m^3(STP) · m/m^2 · s · kPa
q = vapor volumetric flux across the membrane at STP, m^3(STP)/m^2 · s
t = thickness of porous support, m
v_{stp} = molar volume of vapor at STP, m^3(STP)/gmol
x = mole fraction in liquid phase
y = mole fraction in gas phase

Greek letters

α = separation factor relative to methane
ϵ = porosity of porous support
τ = tortuosity of porous support

Subscripts

i = species i
m = in the membrane
o = oil
p = permeate
r = retentate

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