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Skin Thickness of Dense Asymmetric or Composite Membranes for Maximum Extent of Separation of Permanent Gas Mixtures

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Abstract

The dense skin thickness in a dense asymmetric polymeric membrane of the Loeb-Sourirajan type has been optimized for achieving the maximum extent of separation of a binary mixture of permanent gases with the help of Sirkar's expression for the extent of separation in a single entry barrier separation stage. The expression for fluxes and separation factor through the dense asymmetric membrane were obtained from a recent analysis by Sirkar. The dense skin thickness on the microporous support in a composite membrane has also been optimized.

For the separation of permanent gas mixtures, dense asymmetric membranes have the inherent advantages of both homogeneous as well as microporous membranes (*1*, *2*). Dense asymmetric membranes can have high separation factors compared to microporous membranes with Knudsen flow through the pores. In addition, the extremely thin but dense skin supported on a microporous backing in a dense asymmetric membrane allows a much higher species flux for the same pressure gradient imposed

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on a completely dense film which cannot be used with a thickness of less than about 1 mil. An approximate theory of separation of permanent gas mixtures through such dense asymmetric polymeric membranes, which are predominantly of the type of Loeb-Sourirajan CA membranes, has been recently developed by Sirkar (*2*). Sirkar (*2*) has shown that an acceptable expression for the ideal separation factor of permanent gas Species 1 and 2 through a dense asymmetric membrane is

$$\alpha_{12} = \left(\frac{P_{1m}}{P_{2m}}\right)\left(\frac{\delta_2}{\delta_1}\right)\left[\frac{1 + (P_{2m}/\bar{a}_0)\sqrt{M_2}\{(l/\delta_2) - 1\}}{1 + (P_{1m}/\bar{a}_0)\sqrt{M_1}\{(l/\delta_1) - 1\}}\right] \tag{1}$$

where P_{im} is the permeability coefficient of *i*th species through a completely dense membrane of the same polymer, δ_i is the operational skin thickness of *i*th gas species in the asymmetric membrane of total thickness l, M_i is the molecular weight of the *i*th species, and $\bar{a}_0$ is the coefficient in the flux expression for Knudsen flow in the microporous backing as given by

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$$N_{il} = P_{im}\frac{(p_{i0} - p_i\delta_i)}{\delta_i} \tag{1a}$$

$$= \frac{\bar{a}_0}{\sqrt{M_i}}\frac{(p_i\delta_i - p_{il})}{(l - \delta_i)} \tag{1b}$$

$$= \frac{(p_{i0} - p_{il})}{\left[\dfrac{\delta_i}{P_{im}} + \dfrac{\sqrt{M_i}(l - \delta_i)}{\bar{a}_0}\right]} \tag{1c}$$

Here the partial pressure of *i*th species at the high-pressure feed surface, skin-backing interface, and low pressure surface of the film are p_{i0}, $p_i\delta_i$, and p_{il}, respectively. The individual species flux expression (1c) and Eq. (1) for α_{12} indicate that as the thickness of the dense skin in the asymmetric membrane of length l increases, the species flux decreases but the separation factor increases. In any barrier separation process the process objective is to achieve maximum amount of separation. This need not coincide with the conditions leading to a maximum possible separation factor in a single-stage operation unless certain purity constraints are imposed on the light fraction in a single stage itself. It is known that the universal separation index, the extent of separation ξ, developed by Rony (*3*), is a better indicator of the amount of separation than the separation factor. Sirkar (*4*) has shown in a generalized manner that Rony's extent of separation ξ is a composite index of separation consisting of a product of a capacity factor and the enrichment factor $(\alpha - 1)$. For a barrier separation stage, the expression for the extent of separation ξ from Sirkar (*4*) is

$$\xi = \left[\frac{\dot{n}_{21}}{\dot{F}_k f_{2k}}\right] \text{abs}\left(\frac{x_{11} f_{2k}}{x_{21} f_{1k}} - 1\right) \quad (2)$$

For a very small stage of length *dl*, the above expression may be simplified to

$$\xi = \left[\frac{N_{21}\, dl}{\dot{F}_k f_{2k}}\right] \text{abs}\,(\alpha_{12} - 1) \quad (3)$$

where N_{21} is the flux of heavy Species 2 through the barrier in a stage fed with a stream of mole fraction f_{ik} at a molar flow rate $\dot{F}_k$, and x_{ij} is the mole fraction of *i*th species in region *j*. Region 1 refers to the permeate region and 2 refers to the feed region. The first factor in Expression (3) for ξ is the capacity factor. Now, from Eq. (1c), as the dense skin thickness δ_i increases, the flux N_{21} decreases and the flux N_{11} decreases also:

$$N_{21} = \frac{(p_{20} - p_{2l})}{\left[\dfrac{\delta_2}{P_{2m}} + \dfrac{\sqrt{M_2}(l - \delta_2)}{\bar{a}_0}\right]} \quad (4)$$

whereas the separation factor α_{12} increases as δ_i increases. Thus it would be appropriate to determine the skin thickness in a dense asymmetric membrane which maximizes the index, ξ, the extent of separation which is essentially a product of the two quantities N_{21} and $(\alpha_{12} - 1)$. Such a step acquires greater relevance with dense composite membranes where a dense polymeric skin of controlled thickness could be coated onto a microporous substrate of required porosity, pore sizes, and rigidity. Riley, Hightower, and Lyons (*5*) have already prepared dense skins of thickness varying between 200 and 2000 Å from cellulose acetates of various degrees of substitution supported on microporous CN–CA surfaces. Therefore, the dense skin thickness on a microporous substrate in a composite membrane should also be determined for achieving maximum extent of separation.

For a composite membrane with a dense skin coating on a microporous support, micropore dimensions are likely to increase abruptly on the surface (*6*) unlike the smooth transition in dense asymmetric films. The flux equations through the skin and the support are then, respectively,

$$N_{il} = P_{im}[(p_{i0} - p_{i\delta})/\delta] \quad (5)$$

$$= \frac{a_0}{\sqrt{M_i}} d_{pb} \in \left[\frac{(p_{i\delta} - p_{il})}{(l - \delta)}\right] \quad (6)$$

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so that under conditions of $p_{1l} \ll p_{10}$ and $p_{2l} \ll p_{20}$ necessary for obtaining the ideal separation factor, we get

$$\alpha_{12} = \frac{p_{1l}p_{20}}{p_{2l}p_{10}} = \left(\frac{P_{1m}}{P_{2m}}\right)\left[\frac{1 + \frac{\sqrt{M_2}P_{2m}}{a_7}\left(\frac{1}{\delta} - 1\right)}{1 + \frac{\sqrt{M_1}P_{1m}}{a_7}\left(\frac{1}{\delta} - 1\right)}\right] \tag{7}$$

where d_{pb} is an average pore diameter of the support at the interface where the porosity is ε. Assuming

$$a_0 d_{pb}\varepsilon = a_7 \tag{8}$$

the expression for the extent of separation for the case of a composite membrane with a dense skin becomes

$$\xi = \left[\frac{dl(p_{10} + p_{20})}{\dot{F}_k}\right]\left[\frac{1}{\frac{\delta}{P_{2m}} + \frac{\sqrt{M_2}(l - \delta)}{a_7}}\right] \text{abs}\left|\frac{\frac{1}{P_{2m}} + \frac{\sqrt{M_2}}{a_7}\left(\frac{l}{\delta} - 1\right)}{\frac{1}{P_{1m}} + \frac{\sqrt{M_1}}{a_7}\left(\frac{l}{\delta} - 1\right)} - 1\right| \tag{9}$$

Here we have assumed that $f_{2k} \cong (p_{20}/p_{20} + p_{10})$ and $p_{20} \gg p_{2l}$. Simplifying Expression (9) to

$$\xi = \left[\frac{dl(p_{10} + p_{20})}{\dot{F}_k}\right] \cdot \text{abs}\left|\frac{1}{\delta\left[\frac{1}{P_{1m}} + \frac{\sqrt{M_1}}{a_7}\left(\frac{l}{\delta} - 1\right)\right]} - \frac{1}{\delta\left[\frac{1}{P_{2m}} + \frac{\sqrt{M_2}}{a_7}\left(\frac{l}{\delta} - 1\right)\right]}\right| \tag{10}$$

and equating $(d\xi/d\delta)$ from Expression (10) to zero, we obtain the relation

$$\frac{\left[\frac{\delta}{P_{2m}} + \frac{\sqrt{M_2}}{a_7}(l - \delta)\right]^2}{\left[\frac{\delta}{P_{1m}} + \frac{\sqrt{M_1}}{a_7}(l - \delta)\right]^2} = \frac{\frac{1}{P_{2m}} - \frac{\sqrt{M_2}}{a_7}}{\frac{1}{P_{1m}} - \frac{\sqrt{M_1}}{a_7}} \tag{11}$$

from which

$$(\alpha_{12}|_{\xi_{opt}})^2 = \frac{\frac{1}{P_{2m}} - \frac{\sqrt{M_2}}{a_7}}{\frac{1}{P_{1m}} - \frac{\sqrt{M_1}}{a_7}} \tag{12}$$

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The value of the dense skin thickness δ on the microporous support of a composite membrane may be obtained from Relation (12) and the Definition (7) of α_{12} as

$$\frac{\delta}{l} = \frac{\left[\dfrac{\dfrac{\sqrt{M_1}}{a_7}}{\left\{\dfrac{1}{P_{1m}} - \dfrac{\sqrt{M_1}}{a_7}\right\}^{1/2}} - \dfrac{\dfrac{\sqrt{M_2}}{a_7}}{\left\{\dfrac{1}{P_{2m}} - \dfrac{\sqrt{M_2}}{a_7}\right\}^{1/2}}\right]}{\left[\left\{\dfrac{1}{P_{2m}} - \dfrac{\sqrt{M_2}}{a_7}\right\}^{1/2} - \left\{\dfrac{1}{P_{1m}} - \dfrac{\sqrt{M_1}}{a_7}\right\}^{1/2}\right]} \tag{13}$$

when the extent of separation has the maximum value. Since the flux N_{i1} of the ith species through a composite membrane is going through the dense skin and then the microporous support, it is obvious that

$$\frac{a_7}{\sqrt{M_i}} \gg P_{im} \tag{14}$$

since

$$(dp_i/dx)_{\text{skin}} \gg (dp_i/dx)_{\text{backing}}$$

This allows Relation (13) to be simplified further to

$$\left.\frac{\delta}{l}\right|_{\xi_{\text{opt}}} = \left(\frac{P_{2m}\sqrt{M_2}}{a_7}\right) \frac{\left\{\left(\dfrac{P_{1m}}{P_{2m}}\right)^{1/3}\left(\dfrac{M_1}{M_2}\right)^{1/2} - 1\right\}}{\left\{\left(\dfrac{P_{1m}}{P_{2m}}\right)^{1/2} - 1\right\}} \left(\frac{P_{1m}}{P_{2m}}\right)^{1/2} \tag{15}$$

where we have assumed that $1 - (\sqrt{M_i}P_{im}/a_7) \cong 1$. Thus the value of δ for obtaining ξ_{opt} may be obtained if a_7, P_{1m}, and P_{2m} are known for a dense composite membrane. It may be noted that Lee (*7*) has dealt with the permeation properties of laminated membranes in general without considering the aspect of maximizing separations.

For a dense asymmetric membrane, Sirkar (*2*) has shown that a dense skin of constant thickness independent of the gas species does not adequately describe the gas permeation data of Gantzel and Merten (*1*) through a Loeb-Sourirajan type of CA membranes. Sirkar's model with the "operational skin thickness" δ_i varying with the gas species appeared to describe the data of Ref. 1 much better. The maximization of the extent of separation for a dense asymmetric membrane should therefore be based on

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$$\xi = \left[\frac{dl(p_{10} + p_{20})}{\dot{F}_k}\right]\left[\frac{1}{\dfrac{\delta_2}{P_{2m}} + \dfrac{\sqrt{M_2}(l - \delta_2)}{\bar{a}_0}}\right]$$

$$\cdot \text{abs}\left|\frac{\dfrac{\delta_2}{P_{2m}} + \dfrac{\sqrt{M_2}(l - \delta_2)}{\bar{a}_0}}{\dfrac{\delta_1}{P_{1m}} + \dfrac{\sqrt{M_1}(l - \delta_1)}{\bar{a}_0}} - 1\right| \tag{16}$$

However, since δ_2 and δ_1 are related and various types of relations have been postulated by Sirkar (*2*), we will adopt one of these for the sake of illustration. Sirkar's (*2*) one-constant linear pore size variation model for the dense skin leads to

$$(\delta_i/\delta_j) = (d_i/d_j) \tag{17}$$

where d_i, d_j are the collision diameters of the species i and j, respectively. Expressing δ_2 as $(\delta_2/\delta_1)\delta_1 = (d_2/d_1)\delta_1$, we can obtain from Expression (16) for $(d\xi/d\delta_1) = 0$

$$\frac{\left[\dfrac{\delta_2}{P_{2m}} + \dfrac{\sqrt{M_2}}{\bar{a}_0}(l - \delta_2)\right]^2}{\left[\dfrac{\delta_1}{P_{1m}} + \dfrac{\sqrt{M_1}}{\bar{a}_0}(l - \delta_1)\right]^2} = \frac{\left[\dfrac{1}{P_{2m}} - \dfrac{\sqrt{M_2}}{\bar{a}_0}\right]\dfrac{d_2}{d_1}}{\left[\dfrac{1}{P_{1m}} - \dfrac{\sqrt{M_1}}{\bar{a}_0}\right]} \tag{18}$$

The separation factor under such conditions is given by

$$(\alpha_{12}|_{\xi_{\text{opt}}})^2 = \frac{\left[\dfrac{1}{P_{2m}} - \dfrac{\sqrt{M_2}}{\bar{a}_0}\right]\dfrac{d_2}{d_1}}{\left[\dfrac{1}{P_{1m}} - \dfrac{\sqrt{M_1}}{\bar{a}_0}\right]} \tag{19}$$

Assuming $l \gg \delta_i$ which holds true for most common dense asymmetric membranes, we obtain the following expression for the skin thickness δ_1:

$$\left.\frac{\delta_1}{l}\right|_{\xi_{\text{opt}}} = \frac{\left\{\dfrac{\sqrt{M_2}}{\bar{a}_0}\left(\dfrac{1}{P_{1m}} - \dfrac{\sqrt{M_1}}{\bar{a}_0}\right)^{1/2} - \dfrac{\sqrt{M_1}}{\bar{a}_0}\left(\dfrac{d_2}{d_1}\right)^{1/2}\left(\dfrac{1}{P_{2m}} - \dfrac{\sqrt{M_2}}{\bar{a}_0}\right)^{1/2}\right\}}{\left\{\dfrac{1}{P_{1m}}\left(\dfrac{1}{P_{2m}} - \dfrac{\sqrt{M_2}}{\bar{a}_0}\right)^{1/2}\left(\dfrac{d_2}{d_1}\right)^{1/2} - \left(\dfrac{d_2}{d_1}\right)\dfrac{1}{P_{2m}}\left(\dfrac{1}{P_{1m}} - \dfrac{\sqrt{M_1}}{\bar{a}_0}\right)^{1/2}\right\}} \tag{20}$$

Under the assumptions similar to those leading to Relation (14),

$$\frac{\bar{a}_0}{\sqrt{M_i}} \gg P_{im} \Rightarrow \frac{1}{P_{im}} \gg \frac{\sqrt{M_i}}{\bar{a}_0} \tag{21}$$

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We obtain

$$\left.\frac{\delta_1}{l}\right|_{\xi_{opt}} = \left(\frac{P_{2m}\sqrt{M_2}}{\bar{a}_0}\right)\left(\frac{P_{1m}}{P_{2m}}\right)^{1/2} \frac{\left\{\left(\frac{P_{1m}}{P_{2m}}\right)^{1/2}\left(\frac{M_1}{M_2}\right)^{1/2}\left(\frac{d_2}{d_1}\right)^{1/2} - 1\right\}}{\left\{\left(\frac{P_{1m}}{P_{2m}}\right)^{1/2}\left(\frac{d_2}{d_1}\right)^{1/2} - 1\right\}} \tag{22}$$

for a dense asymmetric membrane.

The permeability coefficients P_{im} through a dense membrane are available for many permanent gases for most polymers. However, the value of $\bar{a}_0$ for the microporous membrane beginning at the interface in a dense asymmetric membrane or the value of a_7 for the microporous backing in the composite membrane is not known. So explicit estimates of (δ_1/l) or (δ/l) are not possible. Experimental determination of $\bar{a}_0$ or a_7 is thus quite necessary.

Determination of the skin thickness optimizing the extent of separation should be carried out along with an economic analysis about the trade-off between flux and separation factor. Previously, trade-off between flux and rejection meant changing the dense polymeric film itself, which may no longer be necessary. One may now choose a polymeric material with an inherently high separation factor as a dense film and then optimize the dense skin thickness in an asymmetric film of the same polymer for optimum separation.

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