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BINARY GAS MIXTURE SEPARATION IN DUAL PERMEATORS WITH PERMEATE RECYCLES

GORAN T. VLADISAVLJEVIĆ and MILOŠ B. RAJKOVIĆ

(Institute of Food Technology, Faculty of Agriculture, University of Belgrade, P.O.Box 127, YU-11081 Belgrade-Zemun, YUGOSLAVIA)

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Mathematical models of perfectly mixed dual permeators with permeate recycles, operating with zero reject flow rate and zero permeate pressures (γ' = γ'' = 0), have been developed. The equations for determination of the permeate compositions, the membrane area requirements and the separation factors have been derived, taking into consideration two different cases, one permeate recycle and two simultaneous permeate recycle streams. The simulation results have been presented for the separation of a CO₂ / H₂ mixture in a permeator enclosing both silicone rubber and cellulose acetate membranes. As silicone rubber membrane is more permeable to CO₂ than to H₂, while the opposite is true for a cellulose acetate membrane.

Keywords: Dual permeators; Gas separations; Permeate recycle; Silicone rubber membrane; Cellulose acetate membrane

Introduction

Membrane modules usually enclose a single type of membrane, permitting only a binary mixture to be completely separated. The complete separation of an n-component mixture is only possible in a module having n-1 membranes each being preferentially permeable to a different component [1,2]. A permeation unit containing two different kinds of membrane in a single module is called dual or asymmetric permeator [3]. The dual permeator for gas separation was first introduced by Kimura et al. [4] and Ohno et al. [5].

They studied the separation of a N₂/Kr mixture in a perfectly mixed dual cell operating with zero reject flow rate. Sirkar [6] has extended this concept to ternary gas mixture separation in a perfectly mixed and cross-flow dual permeator for finite reject flow rate. Sengupta and Sirkar [7] numerically modelled ternary gas mixture separation in a dual permeator for cross, parallel, countercurrent, and perfectly mixed flow patterns. The mathematical models developed in the above papers are verified by experimental results of several authors [8-10]. Recently, Tekač et al.[11] has shown the applicability of the two-membrane concept to perfectly mixed membrane reactor for reversible gas phase reactions. Until now, most studies concerning permeate recycling have been focused on single-membrane permeators [12-16]. However, a dual permeator with permeate recycle has not yet been investigated.

This paper deals with binary gas mixture separation in a perfectly mixed dual permeator with permeate recycles into the feed stream. Special attention has been paid to the permeate recycle ratios that provide the symmetric separation effects to be obtained, because such effects are of particular interest in a multi-stage cascade operation.

Theory

Dual Permeator with one Permeate Recycle

Consider a binary gas mixture separation in a dual permeator containing two different types of membranes, M' and M". Suppose gas A preferentially goes through membrane M' and gas B through membrane M". Suppose further that M" is less selective toward gas B relative to A than M' toward gas A relative to B. Therefore, a part of the permeate from M" must be recycled to the feed stream in order to enhance the enrichment of B in the permeate from M".

A material balance equation on gas component A at the mixing point designated by a dotted line in Fig.1, is given by

\[ L_A x_1 + L'' A y'' = (L_A + L'' A) z \] (1)
where $L_f$ is the feed molar flow rate, $L^\prime$ is the membrane permeate molar flow rate, $x_f$ is the mole fraction of A in the feed, $y_e$ is the mole fraction of A in the permeate from M, and $z$ is the mole fraction of A in the mixture at the module inlet ($x_f > z > y_e$). Since perfect mixing conditions are assumed, $z$ is also the mole fraction of A in the unpermeated stream everywhere in a module.

By using the definition of the permeate cuts

$$
\theta^* = 1 - \theta = \frac{L_f^\prime}{L_f} = \frac{y_e - y_f}{y_e - y_e}
$$

we obtain from Eq.(1)

$$
z = \frac{y_e + \xi^\prime \theta^* y_e}{1 + \xi^\prime \theta^*}
$$

where $V_e^\prime$ is the molar flow rate of M' permeate at the permeator outlet, and $\xi^\prime$ is the recycle ratio of M' permeate ($\xi^\prime = L_f^\prime / V_e^\prime$).

Consider the case of zero pressure ratios ($\gamma' = \gamma'' = 0$), because in this case the maximum separation factors are obtained [7]. Thus

$$
z = \frac{y_e}{\alpha^* (1 - y_e) + y_e} = \frac{y_e}{\alpha^* (1 - y_e) + y_e}
$$

where $\alpha^* = Q_A^0 / Q_B^0$ and $\alpha'' = Q_A^0 / Q_B^0$ are the selectivity of membranes M' and M'', respectively, and $y_e^*$ is the mole fraction of species A in the permeate produced by membrane M'. Eqs.(2), (3), and (4) are the set of four linear algebraic equations with eight unknowns, and therefore four variables must be specified. If $\alpha^*$, $\alpha''$, $x_f$, and $\xi^\prime$ are known variables, the permeate compositions are as follows

$$
a = \xi^\prime (1 - \alpha^*)[\alpha^* - x_f (\alpha^* - \alpha'')];
$$

$$
b = (\alpha'' - \alpha^*)[1 - x_f (1 - \alpha'')]$$

Accordingly, the depletion separation factor is given by

$$
\beta'' = \frac{y_e (1 - x_f)}{(1 - y_e) x_f} = \frac{\alpha^* [\xi^\prime (1 - \alpha^*) + \alpha'' - \alpha^*]}{\xi^\prime (1 - \alpha^*) \alpha^* + \alpha'' - \alpha^*}
$$

Similarly, the enrichment separation factor is defined as

$$
\beta' = \frac{y_e (1 - x_f)}{(1 - y_e) x_f} = \frac{\alpha^* [\xi^\prime (1 - \alpha^*) + \alpha'' - \alpha^*]}{\xi^\prime (1 - \alpha^*) \alpha^* + \alpha'' - \alpha^*}
$$

The permeate recycle ratio, $\xi^\prime$, at which $\beta' = 1/\beta''$ is called the symmetric recycle ratio [5]. When $\xi^\prime < \xi^\prime$, enrichment of gas A in M' permeate exceeds depletion of this gas in M'' permeate, i.e., $\beta' > 1/\beta''$, and vice versa. When $\xi^\prime = \xi^\prime$, Eqs.(7) and (8) give

$$
\xi^\prime = \frac{(\alpha'' - \alpha^*) \sqrt{\alpha^* \alpha'' - 1}}{(1 - \alpha^*) (\alpha'' - \gamma^* \alpha^*)}
$$

Thus, for the idealised case of zero permeate pressures, the permeate recycle ratio at which an inherently asymmetric permeator ($\alpha^* \neq 1/\alpha''$) achieves symmetric separation effects ($\beta' = 1/\beta''$) is only dependent on the selectivity of the two membranes, $\alpha^*$ and $\alpha''$.

**Membrane Area Requirements**

The dimensionless membrane areas can be written as follows

$$
S_n = \frac{A'' Q_B^0 P}{S'' L_f} = \frac{(1 + \xi^\prime) \theta^* y_e}{\alpha^* z}
$$

$$
S_e = \frac{A' Q_B^0 P}{S' L_f} = \frac{\theta^* y_e}{\alpha'' z}
$$

where $A'$ and $S'$ are the effective area and thickness of membrane M', $Q_B^0$ is the permeability coefficient for gas B through membrane M', and $P$ is the total pressure.
on the high-pressure side of the membranes. From Eqs. (2), (3), (4), and (10), one obtains

$$S'' = (\alpha'' - 1)(\xi'' + 1)$$

$$\frac{\xi''(1-\alpha'') [\alpha'' - x_f(\alpha'') - 1] + \alpha'' - \alpha''}{[\xi''(1-\alpha'') + \alpha'' - \alpha''][\xi''(1-\alpha''')\alpha'' + \alpha'' - \alpha''] \xi''} \tag{12}$$

Similarly, from Eqs. (2), (3), (4), and (11), we get

$$S' = (1 - \alpha'') (\xi'' + 1)$$

$$\frac{\xi''(1-\alpha'') [\alpha'' - x_f(\alpha'') - 1] + \alpha'' - \alpha''}{[\xi''(1-\alpha'') + \alpha'' - \alpha'[\xi''(1-\alpha'')\alpha'' + \alpha'' - \alpha''] \xi''} \tag{13}$$

It means that the membrane area requirements increase with the increase of the permeate recycle ratio. However, the ratio of the areas of M' and M'' is independent of the permeate recycle ratio:

$$A'' = \frac{\delta'' Q_{B2}'}{\delta' Q_{B2}'} = \frac{(Q_B' / \delta') (\alpha'' - 1)}{(Q_B / \delta')(1 - \alpha'')} \tag{14}$$

**Dual Permeator with Two Simultaneous Permeate Recycles**

Consider a dual permeator with two permeate recycle streams (Fig. 2) and suppose that \( \alpha'' > 1/\alpha'' \). The material balance equation on gas species A at junction of gas streams, designated by the dotted line in Fig. 2, is given by

$$L_f x_f + L_y y_e + L_y y_e = (L_f + L_y + L_y) z \tag{15}$$

where \( L_y \) is the molar flow rate of recycling stream of membrane M'. In this case, \( z < x_f \) when \( \xi'' < \xi' \), while \( z > x_f \) when \( \xi'' > \xi' \). Thus

$$z = \frac{x_f + \xi'' \theta'' y_e + \xi'' \theta'' y_e}{1 + \theta'' + \xi'' \theta''} \tag{16}$$

where \( L_y = L_y / V_e \) is the M' permeate recycle ratio. The permeate compositions can be obtained by simultaneously solving Eqs. (2), (4), and (16)

$$a = \xi'' (1-\alpha'') [\alpha'' - x_f (\alpha'' - \alpha'')] ;$$

$$b = (\alpha'' - \alpha''') [1 - x_f (1 - \alpha'')]$$

$$y_e = \frac{x_f \alpha'' [\xi'' (1 - \alpha'') + \alpha'' - \alpha'''] + \xi'' (\alpha'' - 1)]}{a + b + \xi'' \alpha'' (\alpha'' - 1)} \tag{17}$$

$$a = \xi'' (\alpha'' - 1) [\alpha'' + x_f (\alpha'' - \alpha'')] ;$$

$$b = (\alpha'' - \alpha'') [1 + x_f (\alpha'' - 1)]$$

$$\beta'' = \frac{x_f \alpha'' [\xi'' (1 - \alpha'') + \alpha'' - \alpha'''] + \xi'' (\alpha'' - 1)]}{a + b + \xi'' \alpha'' (\alpha'' - 1)} \tag{19}$$

$$\beta'' = \frac{\xi'' (1 - \alpha'') \alpha'' + \alpha'' - \alpha''' + \xi'' (\alpha'' - 1)}{(1 - \alpha'') \alpha'' + \alpha'' - \alpha''' + \xi'' \alpha'' (\alpha'' - 1)} \tag{20}$$

The equation for the \( \xi'' \) value at \( \xi'' > 0 \), and for the \( \xi'' \) value at \( \xi'' > 0 \) can be derived from Eqs. (19) and (20)

$$\xi'' = \frac{\xi''(\alpha'' - \sqrt{\alpha''} \alpha'' - \alpha'')}{(1 - \alpha'') (\alpha'' - \sqrt{\alpha''} \alpha'' - \alpha'')} \tag{21}$$

$$\xi'' = \frac{\xi''(\alpha'' - \sqrt{\alpha''} \alpha'' - \alpha'')}{(1 - \alpha'') (\alpha'' - \sqrt{\alpha''} \alpha'' - \alpha'')} \tag{22}$$
Table 1 Specific permeabilities, Q/Δ, of various gases through silicone rubber (S) and cellulose acetate (CA) membrane at 25 °C

<table>
<thead>
<tr>
<th>Species</th>
<th>Silicone Rubber (M')</th>
<th>Cellulose Acetate (M'')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulfide</td>
<td>131.8</td>
<td>274.1</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>42.84</td>
<td>43.86</td>
</tr>
<tr>
<td>Methane</td>
<td>12.52</td>
<td>0.984</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>8.569</td>
<td>65.78</td>
</tr>
<tr>
<td>Helium</td>
<td>4.611</td>
<td>74.01</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>4.480</td>
<td>1.205</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.690</td>
<td>0.820</td>
</tr>
</tbody>
</table>

However, it must be noted that a simultaneous recycle of two permeate streams is of no practical interest since their effects on the separation factors are opposite, so that each case is equivalent to the corresponding case of only one permeate recycle stream. For example, when ξ'' > ξ', it can be demonstrated that

\[
ξ^\prime_0 = \frac{ξ'' - ξ'}{1 + ξ''}
\]

(23)

where ξ''_0 is the recycle ratio of the permeate from M' which gives the identical permeate compositions as two simultaneous permeate recycles, ξ' and ξ''. Similar to that, when ξ' < ξ'',

\[
ξ^\prime_0 = \frac{ξ' - ξ''}{1 + ξ''}
\]

(24)

when ξ' = ξ'', Eqs. (23) and (24) give that ξ''_0 = ξ' = 0, i.e. the effects of two recycles are entirely nullified, and the permeate compositions obtained are the same as with no recycle.

Results and Discussion

Table 1 lists the specific permeabilities of various species through silicone rubber (M') and cellulose acetate (M'') membrane at the temperature of 25 °C [7]. N₂, CH₄, and CO are more permeable to silicone rubber than to cellulose acetate, while the opposite is true for H₂S, CO₂, H₂, and He. Binary gas mixtures which satisfy the criterion of reverse selectivities (α'' > 1, α' < 1) with respect to the membrane pair of interest are given in Table 2. We have restricted ourselves in this study to a CO₂/H₂ mixture with the feed composition of x₀ = 0.5.

In Fig. 3 the CO₂ mole fractions in the product streams, y', y'', and z, are plotted against permeate recycle ratio, ξ' and ξ''. The mole fraction of CO₂ in the permeate from the silicone membrane ranges from 0.5 (at ξ'' = 0) to 0.882 (at ξ'' = 0 and ξ' = 0), while the CO₂ mole fraction in the CA permeate varies from 0.118 (at ξ'' = 0 and ξ' = 0) to 0.5 (at ξ'' = 0 and ξ' = 0). Therefore, a higher depletion of CO₂ in the CA permeate is achieved only at the expense of a lower enrichment of CO₂ in the permeate from the silicone membrane, and vice versa. If the dual permeator operates without any recycle (ξ' = ξ'' = 0), the mole fractions of CO₂ in the two permeate streams are y' = 0.833 and y'' = 0.401.

Fig. 4 shows the enrichment separation factor and the reciprocal of the depletion separation factor as functions of the recycle permeate ratio, ξ' and ξ''. As expected, β' increases with ξ' at ξ'' = 0, while it decreases as ξ'' is increased at ξ' = 0. On the other hand, 1/β'' increases with ξ'' at ξ' = 0, while it decreases with ξ' at ξ'' = 0. The point of intersection of the β' vs. ξ'' and 1/β'' vs. ξ' plots is indicated by S. The abscissa of point S determines ξ'', and the ordinate gives α''. The effect of recycling is more pronounced when the CA permeate is recycled because the cellulose acetate
The areas of the silicone and cellulose acetate membranes, $A'$ and $A''$, are plotted in Fig.5 as functions of $\xi_1$ at $\xi_2 = 0$ and $\xi_2$ at $\xi_1 = 0$. Besides, the total membrane areas, $A_T$, are also plotted here against $\xi_1$ and $\xi_2$. The total pressure on the high-pressure side of the membranes was taken as $P = 5 \times 10^5$ Pa, and the feed flow rate was selected as $L_f = 10$ m$^3$(STP) h$^{-1}$. It can be seen that $A$ increases with increasing either $\xi_1$ or $\xi_2$, as it does $A''$, and approaches a limiting value at an infinitely large permeate recycle ratio ($\xi_1 = \infty$ or $\xi_2 = \infty$). The membrane area requirements are larger when the CA permeate is recycled, at all permeate recycle ratios.

As an example, at $\xi_1 = \infty$ and $\xi_2 = 0$, the area of the silicone membrane is $A' = 2.976$ m$^2$, while at $\xi_2 = \infty$ and $\xi_1 = 0$, the area of the same membrane is 17.366 m$^2$. The reason for the above trend is a much higher flow rate of the mixture entering the module in the second case (78.7 m$^3$(STP) h$^{-1}$ as compared with 13.5 m$^3$(STP) h$^{-1}$ in the first case).

Conclusions

Single-stage separation of binary gas mixtures in perfectly mixed dual permeators with no reject stream and permeate recycle into the feed stream was investigated. The permeate recycle is the effective way to obtain the symmetric separation effects ($\beta' = 1/\beta''$) in an inherently asymmetric permeator ($\alpha'' \neq 1/\alpha''$). For the simplified case of zero ratios of permeate to feed pressures ($\gamma' = \gamma'' = 0$), the symmetric recycle ratio is only dependent on the membrane selectivities, $\alpha''$ and $\alpha''$. The implementation of permeate recycle greatly increases the membrane area requirements since the flow-rate of mixture entering the permeator is increased. The simultaneous recycle of two permeates is of no practical interest since their effects on the permeate compositions are opposite. Therefore, each case is equivalent to the corresponding case of only one permeate recycle.

SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_T$</td>
<td>total membrane area, $A'+A''$, m$^2$</td>
</tr>
<tr>
<td>$A$</td>
<td>individual membrane area, m$^2$</td>
</tr>
<tr>
<td>$L_f$</td>
<td>feed molar flow rate, mol s$^{-1}$</td>
</tr>
<tr>
<td>$L_r$</td>
<td>permeate recycle stream molar flow rate, mol s$^{-1}$</td>
</tr>
<tr>
<td>$P$</td>
<td>total pressure on the high-pressure side of membranes, Pa</td>
</tr>
<tr>
<td>$Q$</td>
<td>permeability coefficient, mol m$^{-1}$ Pa$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$Q/\delta$</td>
<td>specific permeability, mol m$^2$ Pa$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$S$</td>
<td>dimensionless membrane area, -</td>
</tr>
</tbody>
</table>

Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha''$</td>
<td>membrane selectivity (ideal separation factor), -</td>
</tr>
<tr>
<td>$\beta'$</td>
<td>enrichment separation factor, -</td>
</tr>
<tr>
<td>$\beta''$</td>
<td>depletion separation factor, -</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>ratio of permeate pressure to feed side pressure, -</td>
</tr>
<tr>
<td>$\delta$</td>
<td>membrane thickness, m</td>
</tr>
<tr>
<td>$\theta$</td>
<td>permeate cut (fraction of feed permeated), $V_r/L_f$</td>
</tr>
<tr>
<td>$\xi$</td>
<td>permeate recycle ratio, $L_r/V_e$</td>
</tr>
<tr>
<td>$\xi'$</td>
<td>permeate recycle ratio for which $\beta' = 1/\beta''$</td>
</tr>
</tbody>
</table>
Indices

membrane M' (membrane more permeable to A than to B)
membrane M" (membrane more permeable to B than to A)
apparent value
A,B component of gas mixture

REFERENCES