



# Pressure ratio and its impact on membrane gas separation processes



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## ABSTRACT

The feed and permeate pressures achievable in most gas separations are limited by economics. As a result, commercial membrane separation processes usually operate with a feed-to-permeate pressure ratio ( $\theta$ ) in the range of 5–15. This limited pressure ratio means that the optimum membrane may not be the one with the highest selectivity; rather, a membrane with lower selectivity, but tailored to the pressure ratio, may result in a more economical process. In other words, when a process is pressure ratio limited, the useful selectivity is also limited. The balance between pressure ratio and selectivity is often ignored by membrane developers. The importance of this balance is illustrated with two applications of current interest: CO<sub>2</sub> capture from power plant flue gas, and dehydration of azeotropic bioethanol.

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## 1. Introduction

Membrane researchers have been aware of the trade-off between selectivity ( $\alpha$ ) and permeability ( $P$ ) since the early days of membrane gas separation technology. Robeson first formulated this trade-off relationship in his influential paper [1]. You can have high selectivity or high permeability, but it is difficult to have both at the same time. Another important and less appreciated membrane parameter is the pressure ratio ( $\theta$ ), defined as

$$\theta = \frac{p^f}{p^p} \quad (1)$$

where  $p^f$  and  $p^p$  are the feed and permeate pressures on either side of the membrane. The impact of pressure ratio on membrane gas separation processes is the subject of this paper.

In many materials research studies, pressure ratio is ignored or treated as a freely adjustable parameter and set at a conveniently high value, where its impact on the separation can be neglected. Unfortunately, in industrial gas separation processes, adjustment of the pressure ratio comes at a significant price in terms of compressor capital cost and power usage. The cost of the compressor package may be much more than the cost of the membrane unit, and the cost of electricity used to power the compressor is usually the largest operating expense. For these reasons, pressure ratios used in industrial processes are normally below 20, and are typically in the range of 5–15.

In this paper, we will use two specific applications to illustrate the importance of pressure ratio and its impact on membrane selection.

- The first application is capture of CO<sub>2</sub> from power plant flue gas. Flue gas from combustion of fossil fuels is produced in enormous volumes and contains 5–15 mol% CO<sub>2</sub> at atmospheric pressure [2,3]. The membrane system must remove 50–90% of this CO<sub>2</sub> in a concentrated stream for sequestration. This is a low pressure separation, so large membrane areas are needed. But the key economic concern is the energy consumed by the compression/vacuum equipment that drives the process. This energy use is directly related to the membrane pressure ratio. A competitive process requires an affordably low pressure ratio, and this determines the preferred membrane selectivity.
- The second application is dehydration of azeotropic ethanol/water mixtures in bioethanol plants. This is the final dehydration step in the production of dry bioethanol and is a large potential market for water-permeable vapor permeation membranes [4]. The objective is to break the azeotrope produced by distillation of the ethanol fermentation broth, reducing the water content from 16 mol% (7 wt%) to 0.76 mol% (0.3 wt%). The permeate vapor is usually cooled and condensed to spontaneously create a vacuum on the permeate side of the membrane, enabling relatively high pressure ratios to be achieved. However, the extreme operating conditions (ethanol/water vapor mixtures at 100–130 °C) require expensive membrane module materials, so controlling membrane area is important. We will show that the balance between pressure ratio and selectivity also affects membrane area.

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## 2. Theoretical basis

Membrane gas permeation is quantified in terms of membrane permeability and selectivity using the solution-diffusion equation:

$$j_i = \frac{P_i}{\ell} (p_i^f - p_i^p) \quad (2)$$

where  $j_i$  is the molar flux ( $\text{cm}^3(\text{STP})/\text{cm}^2 \text{ s}$ ) of component  $i$ ,  $\ell$  is the membrane thickness,  $p_i^f$  and  $p_i^p$  are the partial vapor pressures of component  $i$  on the feed side and permeate side of the membrane, and  $P_i$  is the permeability of the membrane material to component  $i$ , usually expressed in Barrer (where  $1 \text{ Barrer} = 1 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}/\text{cm}^2 \text{ s cmHg}$ ). Because the thickness of the selective layer in composite membranes is often difficult to measure, commercial membranes are typically characterized by their partial pressure normalized flux ( $j_i/\Delta p_i$ ) or permeance ( $P_i/\ell$ ), which is expressed in gas permeation units or gpu (where  $1 \text{ gpu} = 1 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \text{ s cmHg}$ ).

The membrane separation capability, or selectivity, is expressed as the ratio of the permeances or permeabilities of components  $i$  and  $j$ :

$$\alpha_{ij} = \frac{P_i/\ell}{P_j/\ell} = \frac{P_i}{P_j} \quad (3)$$

where  $\alpha_{ij}$  is the selectivity of the membrane for component  $i$  over component  $j$ .

## 3. CO<sub>2</sub>/N<sub>2</sub> separations

By way of illustrating the importance of pressure ratio, consider the one-stage CO<sub>2</sub>/N<sub>2</sub> separation process shown in Fig. 1. For CO<sub>2</sub> to permeate the membrane, the partial pressure of CO<sub>2</sub> in the permeate must be less than the partial pressure of CO<sub>2</sub> in the feed, so we can write:

$$p^p \times \text{permeate CO}_2 \text{ concentration } (C_{\text{CO}_2}^p) \leq p^f \times \text{feed CO}_2 \text{ concentration } (C_{\text{CO}_2}^f) \quad (4)$$

Hence

$$\frac{C_{\text{CO}_2}^p}{C_{\text{CO}_2}^f} \leq \frac{p^f}{p^p} = \theta \quad (5)$$

or

$$\text{membrane enrichment} \leq \text{pressure ratio } (\theta) \quad (6)$$

This simple relation can also be written as

$$\frac{C_{\text{CO}_2}^p}{\theta} \leq C_{\text{CO}_2}^f \quad (7)$$

In the separation shown in Fig. 1, the feed contains 10 mol% CO<sub>2</sub>. From Eq. (5), this means that, at a pressure ratio of 5, the permeate can contain no more than 50 mol% CO<sub>2</sub>. Thus, the rest of the permeate must be nitrogen, the slower permeating component. It follows that the membrane area required to permeate a specific volume of CO<sub>2</sub> at a specific pressure ratio is determined more by the permeation rate of the slow component (nitrogen) than by that of the fast component (CO<sub>2</sub>). In the limit that the permeation rate of the slow component drops to zero (an infinitely selective membrane), no slow component permeates, so an infinite membrane area is required.

The impact of membrane selectivity on membrane performance at a particular pressure ratio is illustrated graphically in Fig. 2; two examples are shown here, one is at pressure ratio of 5, and the other is at pressure ratio of 10. The membranes are assumed to have the same CO<sub>2</sub> permeance of 1000 gpu, and the selectivity is varied by changing the nitrogen permeance. The feed CO<sub>2</sub> concentration is assumed to be 10 mol% and the feed flow rate is 1000 m<sup>3</sup>(STP)/h. This plot and others shown later in this paper could have been calculated using analytical solutions derived by Pan and Habgood in the 1970s [5–7]. However, in this paper, these plots have been generated using differential element membrane code written at MTR and incorporated into a computer process simulation program (ChemCad 6.3, ChemStations, Austin, TX).

First consider the curves in Fig. 2 calculated at a pressure ratio of 5. The plot in Fig. 2(a) shows the permeate CO<sub>2</sub> concentration as a function of increasing membrane selectivity. At a selectivity of 1 (no separation), the permeate concentration is the same as the feed. As the selectivity increases, the permeate concentration increases, reaching about 40 mol% CO<sub>2</sub> at a selectivity of 40. As the selectivity increases further, the permeate concentration approaches the limiting value of 50 mol% given by Eq. (5). Fig. 2 (b) shows the relative membrane area required to permeate a fixed amount of CO<sub>2</sub> at the same conditions used in Fig. 2(a). This plot has an exponential form where the required membrane area increases rapidly as membrane selectivity increases. It follows that at a pressure ratio of 5 the optimum selectivity under the chosen conditions is between about 20 and 40. A higher selectivity produces a slight increase in permeate CO<sub>2</sub> concentration, but at the expense of a very large increase in membrane area (and cost).

Consider now the curves in Fig. 2 calculated at a pressure ratio of 10. As the membrane selectivity increases, the permeate CO<sub>2</sub> concentration increases approaching a limiting value of 100 mol% given by Eq. (5). As before, the membrane area increases with increasing selectivity. Comparing the curves for the two pressure ratios, it is clear that increasing the pressure ratio, if economically possible, has a very beneficial effect: at the same selectivity and CO<sub>2</sub> permeance, a smaller membrane area is needed to produce the same amount of permeate, which has a higher concentration of CO<sub>2</sub>. However, even at

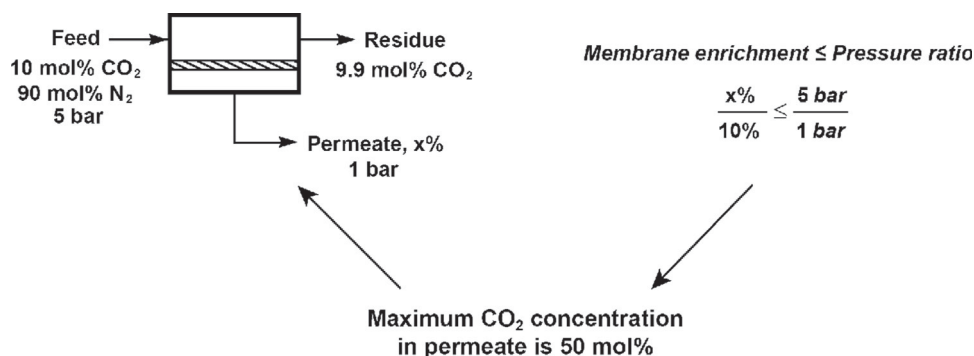


**Fig. 1.** Separation of CO<sub>2</sub> from nitrogen by a CO<sub>2</sub>-selective membrane at a pressure ratio of 5 (5 bar feed, 1 bar permeate). The permeate can never contain more than 50 mol% CO<sub>2</sub>, even when the membrane is infinitely selective.

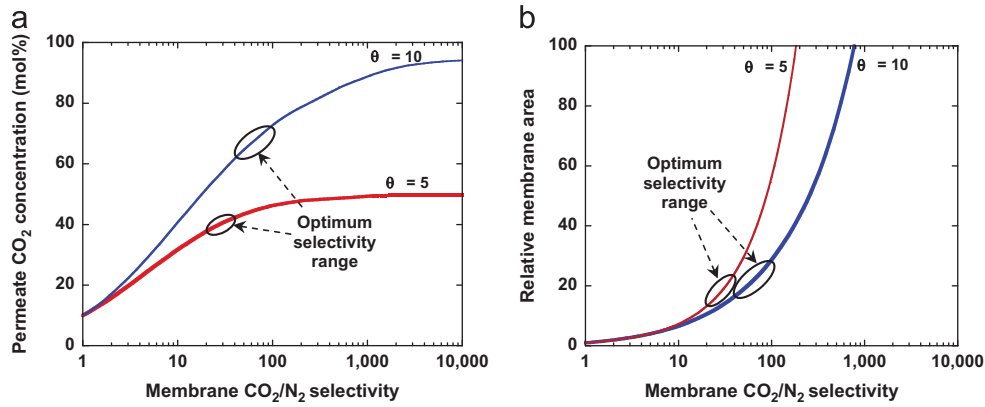


**Fig. 2.** The effect of membrane selectivity and pressure ratio on (a) the permeate CO<sub>2</sub> concentration and (b) the required membrane area, for the separation process illustrated in Fig. 1. In these calculations, CO<sub>2</sub> permeance is fixed at 1000 gpu and selectivity is varied by changing the N<sub>2</sub> permeance. The feed CO<sub>2</sub> concentration is 10 mol%, and feed flow rate is 1000 m<sup>3</sup>(STP)/h.

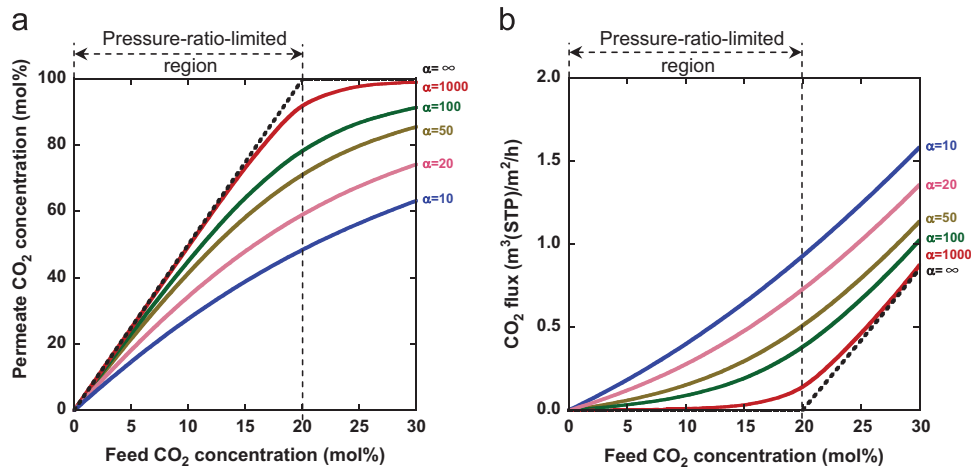


**Fig. 3.** (a) Permeate CO<sub>2</sub> concentration and (b) CO<sub>2</sub> flux at varying feed gas CO<sub>2</sub> concentrations and CO<sub>2</sub>/nitrogen selectivities. All separations are performed at a pressure ratio of 5 (5 bar feed, 1 bar permeate), with membranes having a CO<sub>2</sub> permeance of 1000 gpu, at feed flow rate of 1000 m<sup>3</sup>(STP)/h. There is a trade-off between CO<sub>2</sub> flux and CO<sub>2</sub> concentration in the permeate. The membrane with a selectivity of 10 has the highest flux, but the lowest CO<sub>2</sub> enrichment. The membrane with a selectivity of 1000 has the lowest flux, but the highest enrichment.

the higher pressure ratio of 10, a tradeoff between membrane area and permeate CO<sub>2</sub> concentration remains, with the optimum selectivity now in the range of 40–100.

Another way to illustrate the impact of pressure ratio on the optimum membrane selectivity is shown in Fig. 3. As before, the calculations are made at a fixed CO<sub>2</sub> permeance of 1000 gpu, a feed flow rate of 1000 m<sup>3</sup>(STP)/h, and the selectivity is changed by varying the nitrogen permeance. The pressure ratio is set at 5. The figure shows the changes in permeate CO<sub>2</sub> concentration and CO<sub>2</sub> flux as a function of CO<sub>2</sub> feed concentration and membrane selectivity. The feed concentration is varied from 0–30 mol% CO<sub>2</sub>. A series of curves is shown for membranes with selectivities between 10 and 1000. Good quality polymeric membranes typically have selectivity between 30 and 60 for this gas mixture [2,8], and facilitated transport membranes have been reported with selectivities up to 1000 [9,10], so all of the membranes shown in Fig. 3 are potentially available.

The plots in Fig. 3 are divided into two regions: a pressure-ratio-limited region and a non-pressure-ratio-limited region. The dividing line between these two regions is taken to be the point at which the permeate concentration can theoretically reach 100 mol% CO<sub>2</sub>. From Eq. (7), this feed CO<sub>2</sub> concentration is then:

$$C_{CO_2}^f = \frac{C_{CO_2}^p}{\theta} = \frac{100}{5} \text{ mol\%} = 20 \text{ mol\%} \quad (8)$$

From Eq. (8), the permeate CO<sub>2</sub> concentration cannot reach 100 mol% if the feed CO<sub>2</sub> concentration is below 20 mol%, even with an infinitely selective membrane; to increase the permeate CO<sub>2</sub> concentration, the pressure ratio has to be increased. Hence, at feed concentrations below 20 mol% CO<sub>2</sub>, the separation is pressure ratio limited.

The feed CO<sub>2</sub> concentration given by the term 100/ $\theta$  mol% is a useful, albeit arbitrary marker of the pressure-ratio-region boundary. However, in the pressure-ratio-limited region, there is still some influence of membrane selectivity on separation, as can be seen from Fig. 3. Likewise, outside the pressure-ratio-limited region, the pressure ratio will still exert some influence on the process performance.

Considering Fig. 3(a) first, at a fixed feed concentration, for example 10 mol% CO<sub>2</sub>, the CO<sub>2</sub> enrichment in the permeate increases as the membrane selectivity increases. However, the CO<sub>2</sub> concentration in the permeate soon reaches the limit set by Eq. (5), represented by the line in the figure for an infinitely selective membrane. As a result, the impact of high membrane selectivity on membrane performance is less than what might be expected. At low CO<sub>2</sub> feed concentrations, the difference in permeate CO<sub>2</sub> concentration obtained using a membrane with selectivity of 1000 and one with a selectivity of 50 is small. The benefits of a high selectivity membrane become significant only at

high feed gas CO<sub>2</sub> concentrations, that is, concentrations greater than 20 mol% CO<sub>2</sub>.

The flux data for the same membranes are plotted in Fig. 3(b). All the membranes have the same CO<sub>2</sub> permeance, but the flux is different at different selectivities. The membrane with a selectivity of 10 has the highest CO<sub>2</sub> flux. Membranes with higher selectivities have lower CO<sub>2</sub> fluxes, despite the fact that the CO<sub>2</sub> permeance is unchanged. In reality, the membrane with a selectivity of 10 would normally be 3- to 10-fold more permeable than the membrane with selectivity of 100. This would make the difference in membrane fluxes shown in Fig. 3(b) even more extreme than that shown.

The decrease in CO<sub>2</sub> flux with increasing selectivity is a result of the need to permeate the slow gas, nitrogen. The effect is most marked in the pressure-ratio-limited region, that is, at feed gas CO<sub>2</sub> concentrations below 20 mol%. In this concentration range, a membrane with an infinite selectivity has no flux and the flux of a membrane with a selectivity of 1000 is very small. Practically, this means that using a high selectivity membrane will require a much larger membrane area (and incur much higher cost), without producing much benefit in CO<sub>2</sub> enrichment.

It follows from Fig. 3 that, at a fixed pressure ratio set by the economics of the process, membranes with different selectivities are preferred at different feed concentrations. In the feed concentration range 0–10 mol% CO<sub>2</sub>, a membrane with selectivity between 20 and 50 is probably optimal. A higher selectivity membrane – for example a membrane with selectivity of 100 – might give a slightly higher CO<sub>2</sub> permeate concentration, but, because of the lower flux, would require more than double the membrane area to perform essentially the same separation. In the feed concentration range 10–20 mol% CO<sub>2</sub>, the balance between flux and CO<sub>2</sub> enrichment is optimized with a membrane selectivity of 50–100; at 20–30 mol% CO<sub>2</sub>, the optimum membrane selectivity is around 100–200. Only at feed concentrations above about 30 mol% CO<sub>2</sub> is the highest possible selectivity desirable (subject to the membrane retaining adequate CO<sub>2</sub> permeance). These results suggest that, in an industrial process, membranes of different selectivities might be used in different portions of the plant, depending on the specific concentration of CO<sub>2</sub> in the gas stream being processed.

The separation performance of the high selectivity membranes in Fig. 3 can be improved by increasing the pressure ratio across the

membrane. However, pressure ratios of 20 or 50 – available at the click of a button in a computer simulation – are unrealistic for flue gas CO<sub>2</sub> capture. A few trial calculations show that the maximum affordable pressure ratio is about 10–15; beyond this value, the power consumption for compressors and vacuum pumps becomes a large fraction of the total power output of the plant, making the membrane process completely uneconomical [2].

Another way to approach the flue gas CO<sub>2</sub> capture problem is to use multi-stage processes. Pressure ratio also impacts these designs. Fig. 4 shows a two-stage separation process designed to reduce the CO<sub>2</sub> content of a flue gas stream from 10 mol% to 2 mol%. The permeate from the first membrane unit is recompressed and sent to a second unit. The residue from the second unit is recycled to the front of the process. The first membrane produces a residue stream of 2 mol% CO<sub>2</sub>, achieving a CO<sub>2</sub> removal of 85%. But the permeate is only partially concentrated, to 40–50 mol% CO<sub>2</sub>. The second membrane concentrates the first permeate gas, yielding a twice-enriched CO<sub>2</sub> permeate product stream. The concentration of the second-stage residue stream is set at 10 mol% CO<sub>2</sub>, the same as the feed to which it is recycled, to avoid process inefficiency caused by mixing streams of unequal concentrations.

Two calculations are shown in Fig. 4; one assumes a selectivity of 50, the other a selectivity of 200. The membranes are again assumed to have a CO<sub>2</sub> permeance of 1000 gpu. A pressure ratio of 10 is provided by maintaining 1 bar on the feed side and drawing a vacuum of 0.1 bar on the permeate side. Compressing the feed gas to 10 bar, and keeping the permeate at atmospheric pressure, would produce the same pressure ratio and would significantly reduce the membrane area needed, but at the expense of more power, which is a critical factor in this application [2]. The process shown is sized to treat a flue gas containing 20 t/day of CO<sub>2</sub> at 10 mol% CO<sub>2</sub>, about the amount of flue gas generated by a coal power plant for each MW<sub>e</sub> of electricity produced. The low selectivity process uses about 20% more power and produces a less concentrated CO<sub>2</sub> than the high selectivity process. On the other hand, the membrane area needed for the low selectivity process is only about 1/3 of that used for the high selectivity option (13,760 m<sup>2</sup> vs. 37,120 m<sup>2</sup>).

A design that tries to incorporate the best features of both types of membrane is shown in Fig. 5. The low selectivity membrane ( $\alpha=50$ ) is used for the first membrane stage, which is treating gas containing 2–10 mol% CO<sub>2</sub> (pressure-ratio-limited area). The high

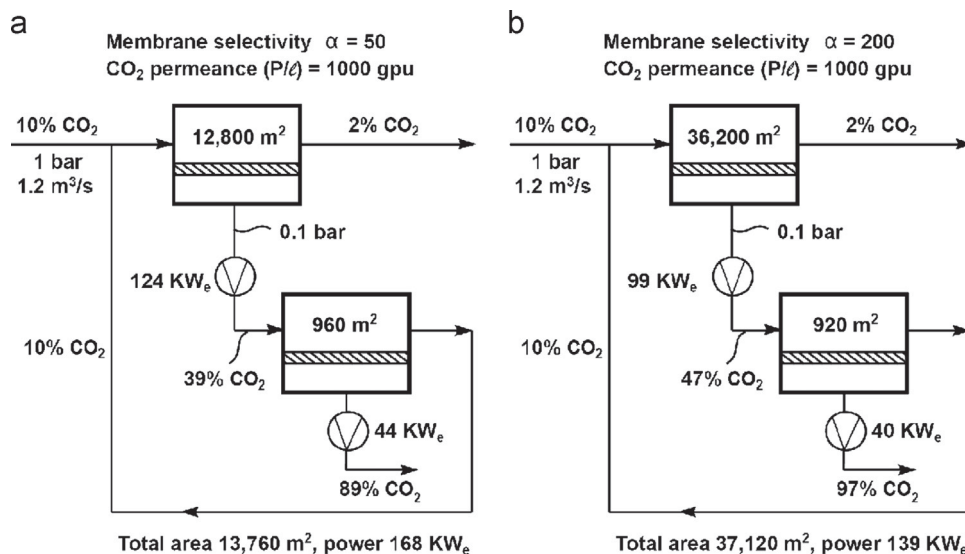


**Fig. 4.** A comparison of two-stage membrane separation systems employing membranes with different CO<sub>2</sub>/N<sub>2</sub> selectivities [50 in Fig. 4(a) and 200 in Fig. 4(b)], but the same CO<sub>2</sub> permeance (1000 gpu) and operating conditions (feed pressure=1 bar, permeate pressure=0.1 bar, pressure ratio=10; feed flow rate=1.2 m<sup>3</sup>/s, vacuum polytropic efficiency=85%). All percentages in the figure are mol%.

selectivity membrane ( $\alpha=200$ ) is used in the second stage, which treats gas containing 10–40 mol%  $\text{CO}_2$  (non-pressure-ratio-limited area). Fig. 5 design produces the same separation as the high selectivity process shown in Fig. 4(b) and uses only 40% of the membrane area, but at the expense of 18% more compression power. The concentration of  $\text{CO}_2$  in the  $\text{CO}_2$  product stream is essentially the same as in Fig. 4(b) process.

Could the process shown in Fig. 5 be improved by changing the pressure ratio? The results of some calculations to answer this question are given in Fig. 6. This figure shows the effect of changing the pressure ratio from 5 to 30. At a pressure ratio of 5, the driving force for separation is low, so the required membrane area is large. The flow of recycle gas from the second stage to the first is high, necessitating large vacuum pumps, and the product quality is poor; the final product only contains 74%  $\text{CO}_2$ .

Increasing the pressure ratio to between 10 and 15 is very beneficial. The higher driving force significantly reduces the membrane area and the size of the vacuum equipment. Simultaneously, the  $\text{CO}_2$  concentration in the product gas increases to 97%. At pressure ratios above 15, the membrane area continues to decrease and the product gas  $\text{CO}_2$  concentration continues to increase, but to a slight degree. However, the vacuum pump power consumption ramps up quickly. Since power consumption is a key parameter, the optimum pressure ratio is chosen to be 10, as was used for Fig. 5 calculations. It is worth noting that even though the second stage of the process operates outside the pressure-ratio-

limited range, the pressure ratio still exerts some influence on the second-stage vacuum power and membrane area requirements, as discussed earlier.

#### 4. Water/ethanol separations

The use of membranes to dehydrate azeotropic water/ethanol vapor mixtures is illustrated in Fig. 7. In this process, the feed to the membrane unit is the overhead vapor from an ethanol/water distillation column. This vapor has a pressure of about 3 bar at 110 °C. The permeate pressure is 0.1 bar, set by the condensation temperature achievable with cooling water, and enabling a relatively high pressure ratio of 30 to be achieved. The membranes available for this separation normally have water/ethanol selectivities in the 20–200 range [11].

Plots that illustrate the effect of water/ethanol selectivity on membrane performance at a pressure ratio of 30 are shown in Fig. 8. These plots are equivalent to those shown in Fig. 3 for  $\text{CO}_2/\text{N}_2$  separation. All the membranes are assumed to have a water permeance of 1000 gpu, and the membrane selectivity is varied from 10 to 1000 by changing the ethanol permeance. The feed flow rate is 1000 kg/h. Fig. 8(a) shows the permeate water concentration as a function of the feed water concentration. The corresponding plot for water flux vs. feed water concentration is shown in Fig. 8(b). As in earlier calculations, we used a constant permeance

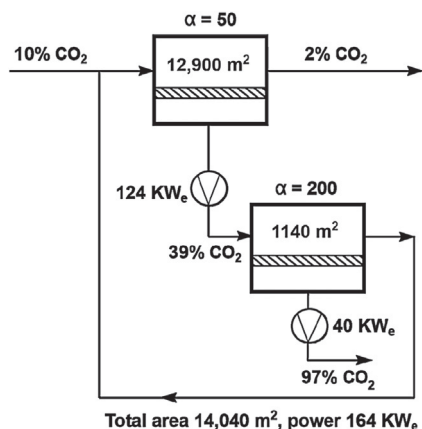


Fig. 5. A two-stage membrane system employing membranes of different selectivity in each stage. The low selectivity membrane is used in the severely pressure-ratio-limited first stage. The high selectivity membrane is used in the second stage, which is not pressure ratio limited, because of the higher feed gas  $\text{CO}_2$  concentration. All percentages in the figure are mol%.

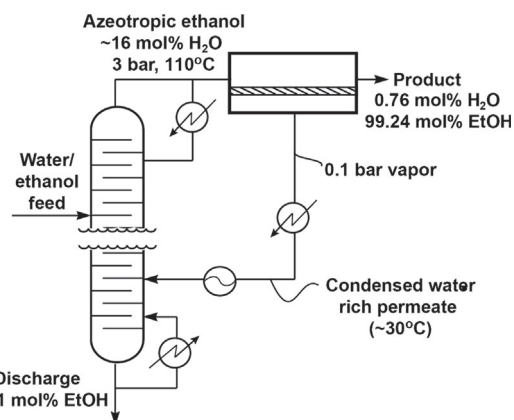


Fig. 7. Simplified block diagram of an ethanol dehydration process. The process uses a water-selective membrane to treat the 3 bar azeotropic water/ethanol mixture overhead vapor produced from the distillation column.

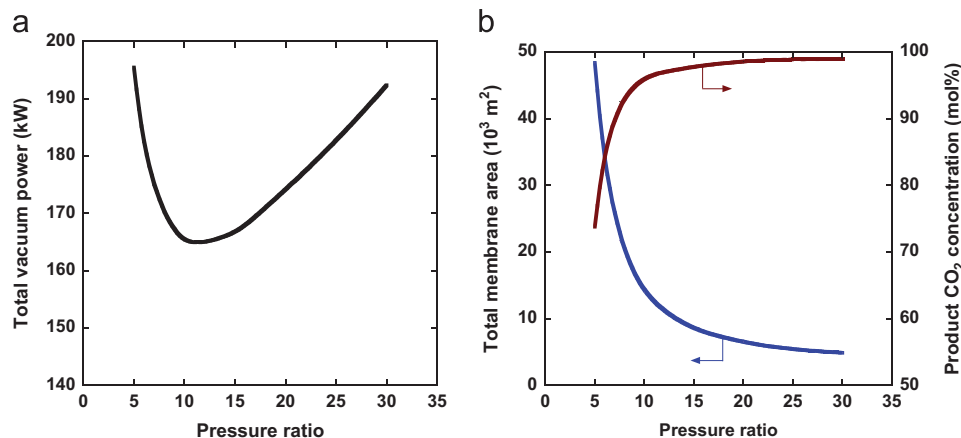


Fig. 6. The effect of pressure ratio on (a) the vacuum power consumption and (b) the membrane area required and the product gas  $\text{CO}_2$  concentration for the process shown in Fig. 5.

for the more permeable component (water) to highlight the change in flux due to pressure ratio limitations.

Fig. 8 shows that, as with the flue gas treatment application, membranes with different selectivities are preferred for different

feed concentrations. When the feed water concentration is greater than about 6–7 mol%, the water fluxes shown in Fig. 8(b) are similar for all selectivities; however, the enrichment of water in the permeate, shown in Fig. 8(a), is much better for the high

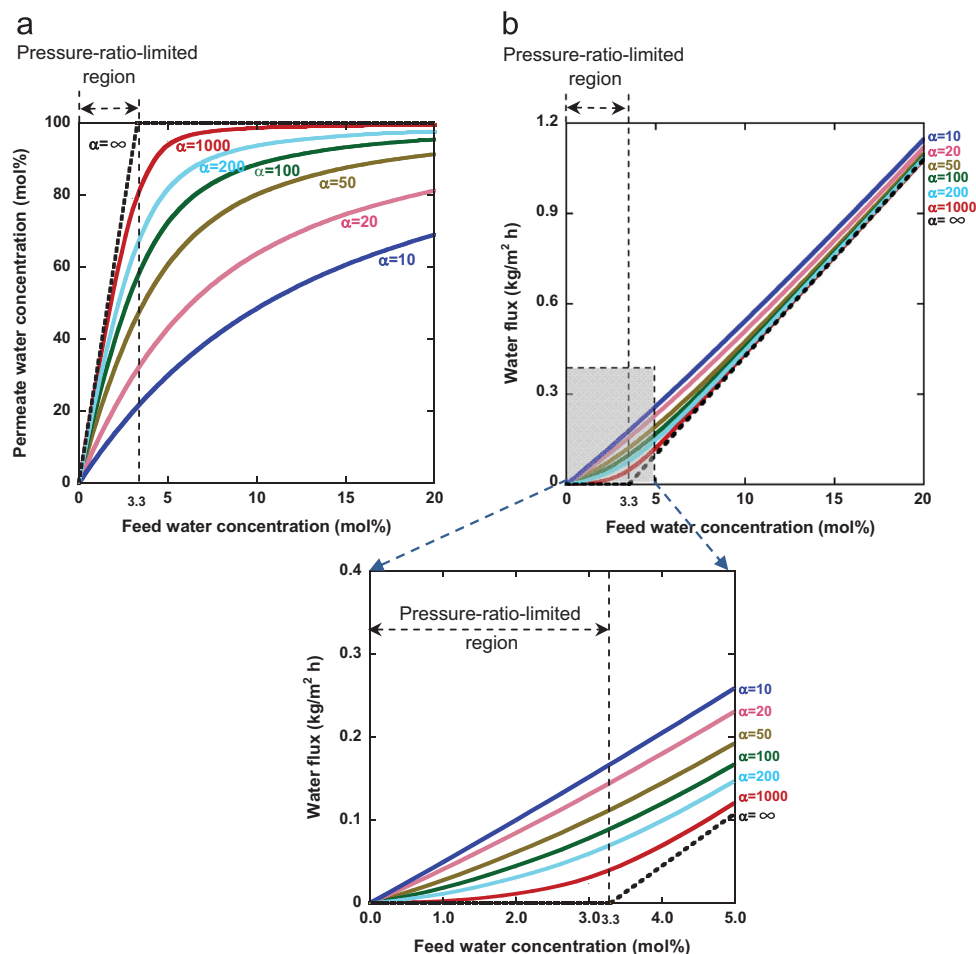


**Fig. 8.** (a) Permeate water concentration and (b) water flux at varying feed water concentrations, for membranes with different water/ethanol selectivities but constant water permeance of 1000 gpu at a feed flow rate of 1000 kg/h. All separations are performed at a pressure ratio of 30 (3 bar feed, 0.1 bar permeate). At this pressure ratio, the process is in the pressure-ratio-limited range at feed water concentrations below 3.3 mol%. There is a trade-off between water flux and water concentration in the permeate. The membrane with a selectivity of 10 has the highest flux, but the lowest permeate water concentration. The membrane with a selectivity of 1000 has the lowest flux, but the highest permeate water concentration.

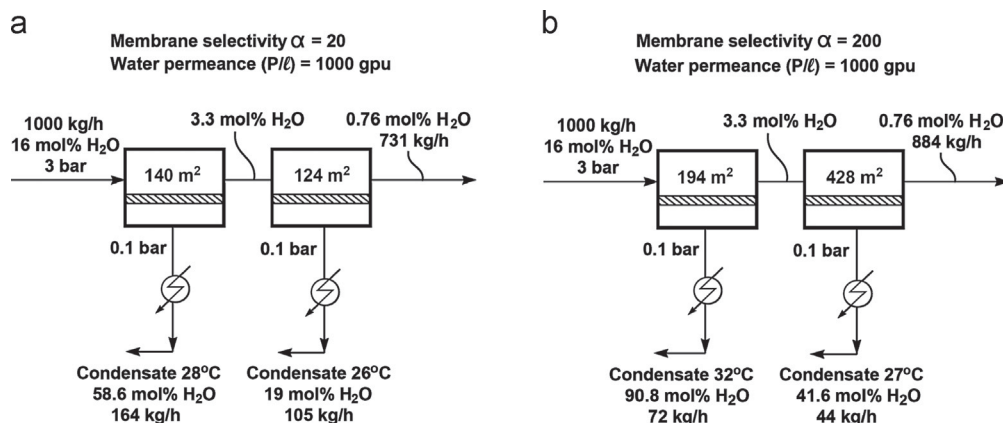


**Fig. 9.** A comparison of two-step membrane separation systems employing membranes with different water/ethanol selectivities of (a) 20 and (b) 200, but the same water permeances ( $P_{H_2O}/l = 1000$  gpu) and operating conditions (feed pressure = 3 bar, permeate pressure = 0.1 bar, pressure ratio = 30; feed flow rate = 1000 kg/h).

selectivity membranes, so the membrane with the highest selectivity available should be used. In contrast, at feed water concentrations below 3.3 mol% the separation is in the pressure-ratio-limited region [from Eq. (8),  $C_{H_2O}^f = C_{H_2O}^p / \theta = 100/30 \text{ mol}\% = 3.3 \text{ mol}\%$ ], and the water fluxes are more affected by membrane selectivity. In this range, membranes with selectivity above 100 have low water fluxes, necessitating the use of large membrane areas. The higher enrichment obtained with high selectivity membranes will not offset the increased cost for the much higher membrane area. Therefore, at feed concentrations below 3.3 mol%, membranes with selectivities between 20 and 100 are preferred. In the intermediate feed concentration range between 3.3 and 6 mol%, membranes with intermediate selectivities between 100 and 200 are optimal.

Some calculations to illustrate how these considerations affect the design of a water/ethanol separation system are provided in Fig. 9. To reach the target ethanol purity, a two-step process is used. The first step, which operates outside the pressure-ratio-limited region, lowers the water concentration from 16 mol% to 3.3 mol%, producing a water-rich permeate that can be recycled to the distillation column. The second step, which operates within the pressure-ratio-limited region, lowers the water concentration in the ethanol product from 3.3 mol% to 0.76 mol%.

Although the amount of water that permeates in the first membrane step is much larger than in the second step, the membrane areas required for each step are comparable. Two sets of calculations are shown in Fig. 9. Fig. 9(a) shows the separation obtained when membranes with a water/ethanol selectivity of 20 are used in both steps; Fig. 9(b) shows the comparable calculations with selectivity of 200. The high selectivity membrane is clearly preferred for the first step. Although the required membrane area is a bit larger (194 m<sup>2</sup> vs. 140 m<sup>2</sup>), the permeate stream contains much more water (90.8 mol% vs. 58.6 mol%) and hence much less ethanol, and is of much smaller volume (72 kg/h vs. 164 kg/h) than when the lower selectivity membrane is used. As a result, ethanol recycle to the distillation column is reduced, improving the overall process efficiency.

The choice of the optimum membrane for the second step is not as clear. The high selectivity membrane produces a significantly better quality permeate (41.6 mol% H<sub>2</sub>O vs. 19 mol%), but uses more than three times the membrane area (428 m<sup>2</sup> vs. 124 m<sup>2</sup>).

The choice becomes easier if the total process as shown in Fig. 10 is considered. In this design, the condensed second-step liquid permeate is pressurized to 3 bar with a pump, re-evaporated and recycled to the incoming feed. The ethanol

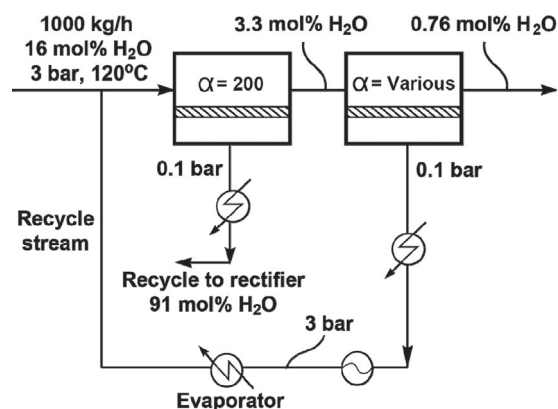


Fig. 10. An integrated process design incorporating membranes of different selectivities, but equal membrane water permeances. Feed pressure 3 bar, permeate pressure 0.1 bar, water permeance 1000 gpu, feed flow rate 1000 kg/h.

concentrations in the feed, first residue and second residue streams are the same as in Fig. 9. The membrane selectivity of the first step is fixed at 200; the second-step selectivity is varied between 5 and 200. Now both the effect of the second membrane selectivity on the second permeate (recycle stream) quality and the interaction of selectivity with pressure ratio can be linked to the total membrane area requirement.

In Fig. 10 process, the mass and water concentration of the recycle stream vary with the selectivity of the second-step membrane. Since the recycle stream is returned to the feed side of the first membrane separation step, performance of this step is also affected. When the selectivity of the second-step membrane is very low, for example 5, the recycle stream is large and contains a large amount of ethanol that is recirculated through the process. Dehydration of the 1000 kg/h feed stream is still possible, but large membrane areas are required for both the first and second membrane steps.

Increasing the selectivity of the second-step membrane from 5 to 20 has a very beneficial effect. The concentration of water in the second-step permeate stream increases and the volume of the stream decreases. The result is to greatly reduce recycle of ethanol and water through the process. The membrane areas required to perform both separation steps are reduced significantly.

When the selectivity of the second-step membrane increases to more than 30, the effect of pressure ratio demonstrated in Fig. 8 becomes apparent. The concentration of water in the second-step permeate continues to increase slowly and the volume of the recycle stream continues to decrease slowly, but these improvements are counteracted by a reduction in the transmembrane water flux, leading to a sharp increase in the second-step membrane area requirement, which becomes very noticeable at selectivities above about 60.

Fig. 11 plots the membrane area (for the first step, second step and total) required to perform the separation as a function of second-step membrane selectivity. The membrane area needed has a broad minimum for second-step membrane selectivities between 10 and 40. When the energy cost of re-evaporating the recycle stream is taken into account, the optimum membrane selectivity is likely to be slightly higher, in the range of 30–50.

The analysis described above shows that this optimized process, like the CO<sub>2</sub> flue gas separation process, requires membranes

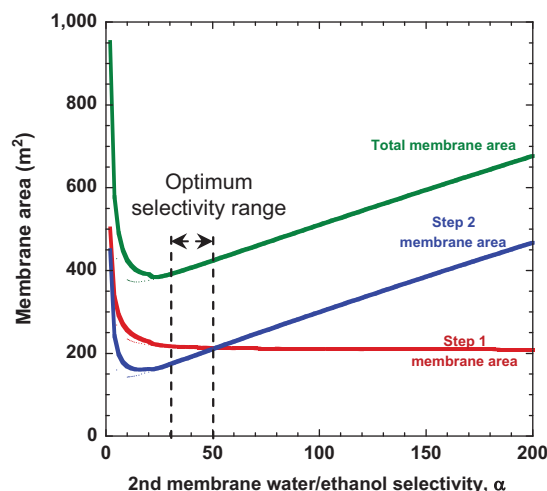


Fig. 11. The membrane areas of the process shown in Fig. 10, as a function of the second-step membrane water/ethanol selectivity. A high selectivity membrane ( $\alpha=200$ ) is preferred for the high feed water concentration, non-pressure-ratio-limited separation performed by the first membrane; a lower selectivity membrane is preferred for the low water concentration, pressure-ratio-limited separation performed by the second membrane unit.

with different properties in different portions of the plant. The analysis also illustrates the importance of considering the operating conditions of the total process when developing membranes for real-world industrial applications.

## 5. Conclusions

*To make useful membranes, you have to understand the process.* In many industrial gas separations, process economics limit the pressure ratio that can be used. As a consequence, the optimum membrane may not be the one with the highest selectivity, and membranes with different selectivities may be preferred in different portions of separation plants. High permeance membranes are always good, but the optimum membrane selectivity depends on the process and the operating conditions, particularly the pressure ratio.

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