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Membrane Systems Engineering for Post-combustion Carbon Capture

Ali Alshehri[b], Rajab Khalilpour[a], Ali Abbas[a]*, Zhiping Lai[b]

[a] School of Chemical and Biomolecular Engineering, The University of Sydney, Sydney, Australia
[b] Advanced Membranes and Porous Materials Center, KAUST, Thuwal, Saudi Arabia

Abstract

This study proposes a strategy for optimal design of hollow fiber membrane networks for post combustion carbon capture from power plant multicomponent flue gas. A mathematical model describing multicomponent gas permeation through a separation membrane was customized into the flowsheet modeling package ASPEN PLUS. An *N*-stage membrane network superstructure was defined considering all possible flowsheeting configurations. An optimization formulation was then developed and solved using an objective function that minimizes the costs associated with operating and capital expenses. For a case study of flue gas feed flow rate of 298 m^3/s with 13% CO_2 and under defined economic parameters, the optimization resulted in the synthesis of a membrane network structure consisting of two stages in series. This optimal design was found while also considering feed and permeate pressures as well as recycle ratios between stages. The cost of carbon capture for this optimal membrane network is estimated to be \$28 per tonne of CO_2 captured, considering a membrane permeance of 1000 GPU and membrane selectivity of 50. Following this approach, a reduction in capture cost to less than \$20 per tonne CO_2 captured is possible if membranes with permeance of 2000 GPU and selectivity higher than 70 materialize.

1. Introduction

Membrane technology is proven as an alternative to high energy consuming separation processes like sea water desalination, air separation and ammonia production. Adapting membrane technology is

* Corresponding author. Tel.: +61 2 9351 3002; fax: +61 2 9351 2854.
E-mail address: ali.abbas@sydney.edu.au (A. Abbas).

attractive to industrial applications for many reasons such as simple operation and low maintenance cost as it does not have moving parts, has relatively low capital cost and small physical footprint which makes it favorable for platform operations and low energy consumption operations. In order to recommend a membrane system for a specific gas separation process it should be proven that it can perform better separation or has better economics than other competing separation processes. Absorption, adsorption, and cryogenic distillation are widely adopted processes for large scale production when high purity and high recovery are required [8]. Nevertheless, these processes are high energy consuming giving room for membrane systems to compete with these processes on an economical basis.

There is general consensus that membranes can perform better for bulk separation. Separation processes can be categorized into two major groups that most industrial applications fall into. The first one is when the concentration of target component (TC) in the inlet feed is high. In such case membranes can perform very well compared to other separation processes, resulting in high purity permeate. But they fail in satisfying retentate with low TC concentration. As an example, we introduce the discussion of natural gas sweetening. Traditionally, the sweetening was carried out with amine-based absorption/desorption processes. In the 1980s, the application of membranes to this process was introduced for the cases where the sour gas concentration is high. Later, it was realized that though membranes are economical for separation of bulk of sour gas, it was not capable of reaching natural gas (retentate) with sour gas concentration less than 2% (enforced by pipeline specifications). Therefore, an amine-membrane hybrid system was introduced; so that the membrane's role is in the bulk separation while the amine-system further reduces the sour concentration of retentate to the target concentration.

The second category is when the concentration of TC in the inlet feed is comparatively low, where at membranes can neither satisfy high purity in permeate stream nor low concentration in retentate stream through a single membrane stage. Therefore, the optimal design that satisfies both recovery and purity will be at higher membrane areas and appropriate pressure. Such arrangements result in higher CAPEX (due to high membrane area) and OPEX (due to high compression costs) making the performance of membranes debatable for such conditions of low concentration feed. In such scenarios, industry has not considered membranes as best available technology (BAT) and have continued to use other separation processes. The selection of appropriate separation options requires detailed techno-economical investigations. The solution for such cases has been a combination of membrane systems consisting of a few stages arranged in parallel or in series to reach higher qualities.

The success and adoption of membrane systems will be, thus, very much dependent on membrane systems engineering. In this paper we present a model-based approach for the systematic synthesis of optimal membrane networks for the carbon capture from combustion flue gas, considering CO_2 / N_2 separation membrane materials (Table1).

Table 1 Examples of different membranes with varying material selectivity and permeance.

Membrane	CO_2/N_2 selectivity	CO_2 permeance (GPU)
Polaris[TM]	50	1000
PVAm/PVA	145	212
Amines/PVA	500	250
Na-Y	100	500
Na-ZSM-5	13.7	870

2. Multi-stage Configuration

As seen in many industrial applications single stage membrane separation has limitation in achieving high quality permeate or retentate while typically the objective of separation is either of these. The reason is due to permeation requiring a driving force between the two membrane sides, i.e. $x_i P_h - y_i P_l > 0$, resulting in:

$$y_i < \frac{x_i P_h}{P_l} = \frac{x_i}{\gamma} \qquad (1)$$

Therefore, when the concentration of TC in the feed is low (x_i), even high pressure ratios (γ) may not achieve high permeate purity (y_i). As such, more stages are required in order to achieve the desired quality and high recovery. The first solution, to best of our knowledge, was a patent by Pfefferle [6] who presented a two stage system with permeate recycle in order to reach high purity permeate. Following the two-stage presentation, a cascade of membrane systems was introduced for a binary gas mixture separation [16, 17]. Gruzdev et al. [18] proposed a method for calculation of a cascade system when there is a multicomponent gas mixture. Some studies have moreover proposed using different membrane materials in the cascade system [21]. The cascade model shown in Fig. 1 is the most general multistage membrane design. This design idea is borrowed from conventional mass transfer operation designs such as multi-stage distillation or extraction systems. The downstream membranes enrich permeate to higher purities of the target components (TCs) while upstream membranes strip remaining traces of TCs to desired values. In many processes either of the enriching or stripping sections is required. For instance in the case of oxygen separation from air in an Air Separation Unit (ASU), the downstream enriching section is not required. In the case of natural gas sweetening, the objective is to minimize concentration of sour gas (CO_2 and H_2S) in retentate. Therefore upstream stripping section is required. Moreover, the concentration of permeate, i.e. sour gas, is also important in order to minimize natural gas loss in permeate stream. Therefore downstream section is also needed.

It is however discussed that, except at very low concentration feed gas, or low-efficient membranes [10], membrane systems consisting of a series of two [16] or three stages [5] are the most techno-economically optimal configurations. It is proven that introduction of more stages, though resulting in slightly less membrane areas and compression energy, the increase in number of compressors ultimately neutralizes this advantage [5].

There have been numerous studies for optimal configurations of two/three-stage membrane systems. Kao et al. [9] compared two systems. One was the so-called continuous column membrane, CMC [6] and the other one was two strippers in series permeator, TSSP. They reported sweet-spot operating condition for each configuration. According to them, TSSP is superior to CMC configuration unless the objective is to minimize membrane area or to have high purity permeate. A similar conclusion was reported by Qiu et al. [15] as a result of economic evaluation stating that TSSP is the most efficient configuration when the objective is high quality retentate while for the case of high quality permeate CMC is more efficient.
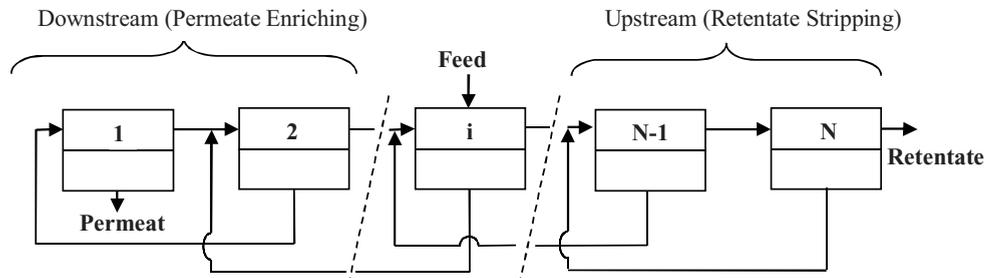

Fig. 1 Schematic of cascade membrane system with recycle.

Bhide and Stern [14] studied seven different one, two and three-stage configurations with respect to minimum costs. They found that a three stage system with a single permeation stage in series with a two-stage permeation cascade with recycle was the best. Pettersen and Lien [5] studied the intrinsic behavior

of several single-stage and multi-stage permeator systems. They also divided the multi-stage system into enriching and stripping cascades which could be two or three-stages. According to them, if the objective is to have retentate with minimum concentration of high permeable component, then the upstream section of cascade (stripping) will be chosen while for high purity permeate product design, downstream section (enriching) is the best choice.

Datta and Sen [7] techno-economically reviewed ten different one-, two- and three-stage configurations for natural gas sweetening. They reported that selection of the best configuration is highly related to feed quality, separation objectives and market values. For example in the case that natural gas price is low, permeate enrichment is not desired while at high natural gas prices, the objective is to minimize natural gas loss in permeate streams with having enrichment stages. According to them, the optimum configuration will be unique in certain range of feed quality, separation policy and market price.

Therefore, it can be concluded that the selection of proper multi-stage system is highly dependent on the separation policy which is mostly affected by economical inputs. When retentate is the target product and its partial loss with permeation is not economically important the policy will be mere stripping. For mere stripping objectives, two-stage (Fig 2b) or three-stage stripper would be selected. However, when the objective is high purity permeate, the policy will be enriching for which two/three-stage enriching system will be the choice.
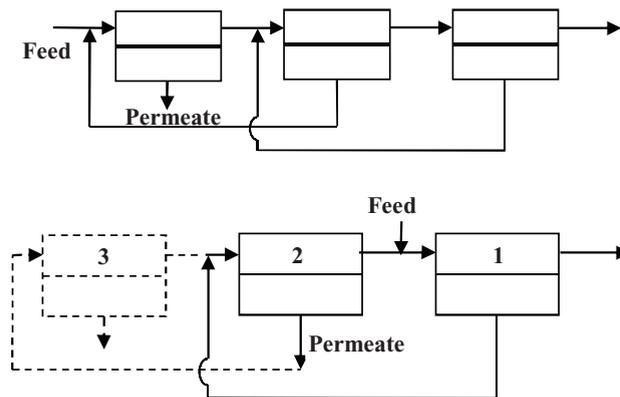

Fig. 2 Schematic of a) three-stage stripping b) two/three-stage enriching systems.

3. Mathematical Model

In this study, we use a multicomponent membrane model for describing separation of CO_2 from flue gas for post combustion carbon capture. It is a general consensus that cross-flow and counter-current flow patterns are the most efficient in terms of removing the high permeable gas. For this reason, we use counter-current flow pattern in the current paper. Khalilpour et al. [13] have reviewed membrane models and concluded that the multicomponent model by Pan [12] is an efficient model. An alternative model, that by Shindo et al. [11] is considered in this paper. This model is applicable to both hollow fiber and flat sheet configurations since it is derived for changes in feed flow rate and components' mole fractions per change in membrane total area then converted to the change in dimensionless area. The limitation of the model by Shindo et al. [11] is, however, the assumption of constant pressure over the membrane length. In this paper we add a description of the permeate pressure change in the fiber lumen. The model equations are listed below:

$$\frac{df}{ds} = -\sum_{k=1}^{n} \alpha_k (x_k - \gamma y_k) \tag{2}$$

$$\frac{dx_i}{ds} = -\frac{\alpha_i}{f}(x_i - \gamma y_i) + \frac{x_i}{f}\sum_{k=1}^{n} \alpha_k (x_k - \gamma y_k) \qquad\qquad i = 1, \cdots, n-1 \tag{3}$$

$$x_n = 1 - \sum_{i=1}^{n-1} x_i \tag{4}$$

$$g = f - (1-\theta) \tag{5}$$

$$y_j = \frac{x_j \, \alpha_{ji}}{\gamma\left[(\alpha_{ji} - 1)\right] + (x_i / y_i)} \qquad\qquad j \neq i, n \qquad if \ g = 0 \tag{6}$$

$$\sum_{k=1}^{n} \frac{x_j \, \alpha_{ji}}{\gamma\left[(\alpha_{ji} - 1)\right] + (x_i / y_i)} = 1 \qquad\qquad j \neq i, n \qquad if \ g = 0 \tag{7}$$

$$y_i = \frac{x_i f - x_{oi}(1-\theta)}{f - (1-\theta)} \qquad\qquad i = 1, \ldots, n \ \ if \ g \neq 0 \tag{8}$$

$$y_n = 1 - \sum_{k=1}^{n-1} x_k \tag{9}$$

Considering a hollow fiber membrane module in which the feed is introduced at the shell side while permeate is collected at the bore side and assuming low velocity of permeate. Then, at low permeate velocity the friction factor is only a function of Reynolds number and can be expressed as:

$$\xi = \frac{64}{R_e} \tag{10}$$

Thus, the Hagen–Poiseuille approximation formula for laminar flow in tubes is applicable in this case but should be derived based on dimensionless area previously considered. Therefore, pressure change in fiber lumen for counter-current flow scheme can be explained as:

$$\frac{dP_i}{dS} = \frac{128 \mu RT(1-f) F_f^2 \delta}{\pi^2 D_i^4 D_o N^2 P_h P_l Q_m} \tag{11}$$

The input data for the model include feed composition and flow rate, process conditions (pressure and temperature), and membrane characteristics which are the membrane thickness, hollow fiber inner and outer diameters and components' permeabilities. The membrane model calculates flow rates and compositions of the gas components in permeate and retentate streams. The set of equations are solved using a Fortran subroutine through backward-difference scheme using Gear's method with adaptive step size.

4. Membrane Network Optimal Configuration

The mathematical model presented in Section 3 was customized into the flowsheet modeling package ASPEN PLUS. In this way the membrane network is readily designed and optimised. An *N*-stage membrane network superstructure was defined considering all possible flowsheeting configurations.

Membrane network efficiency depends on the performance of each permeation unit as well as the network design considering recycle of streams. Finding the optimal design of multi-stage membrane network is non-trivial and without an optimization technique is a near-impossible task as it requires considering all possible configurations at different operating conditions, split ratios and recycle locations.

The optimization function for any chemical process consists mainly of capital (CAPEX) and plant operating (OPEX) expenses. The operational cost is a sum of utilities, labor, maintenance, depreciation of equipment and eventual replacement costs. In the case of membrane gas separation plant the maintenance and labor costs are very low comparable to the power bill. Therefore, these costs can either be ignored or simply added as a fraction of the capital cost. Capital cost is mainly the installation cost of vacuum pumps, compressors, piping system and membrane modules. Capital and operating cost elements considered in this study are listed in Table 2.

The optimization formulation is generated from a combination of objective function, equality and inequality constraints and manipulated (decision) variables. The objective function to be minimized is the membrane network cost ($/tonne of CO_2 captured):

$$\text{Min}: \quad \frac{(P \cdot T \cdot E) + 0.2 \; CC}{M^{CO_2} \; T} \tag{12}$$

where, *P* is the power consumption rate of all network equipment which are either only compressors or a combination of compressors and vacuum pumps. *T* is the hourly operational time per calendar year (h/yr). *E* is the cost of one kilowatt per hour ($/h) and *CC* is the total capital cost of membrane network considered. Multiplying the capture equipment capital cost by 0.2 is based on 5 years of depreciation and interest charges. This assumption is made to be conservative to count for other operating expenses which can be better estimated as a fraction of the plant's capital. M^{CO_2} is the mass flow rate of captured CO_2 (tonne/hr). The cost per tonne of CO_2 captured is a key economic indicator often used to compare different alternative options for mitigation of carbon emissions. The cost parameters which can be used in the objective function are listed in Table 2.

To control the captured CO_2 purity at higher than 90% and also recovering at least 90% mass of CO_2 fed to the membrane network, the following two constraints are added to the optimization formulation:

$$\frac{\sum_{i=1}^{stages} M_i^{CO_2}}{\sum_{i=1}^{stages} M_i} \geq 0.9 \tag{13}$$

$$\frac{\sum_{i=1}^{stages} M_i^{CO_2}}{M_f^{CO_2}} \geq 0.9 \tag{14}$$

Where $M_i^{CO_2}$ is CO_2 mass flow rate of stage *i* product, M_i is total mass flow rate of stage *i* product and $M_f^{CO_2}$ is CO_2 mass flow rate in feed stream. The manipulated variables in the optimization case are the flue gas pressure, permeate pressure, split ratio of permeate streams between product and recycle to previous stages and surface area of each membrane unit. Also, to avoid operating at low pressure the minimum practical operating limit is set for all streams to 0.1 bar [19]. Feed specifications and membrane material separation characteristics are listed in Table 3.

Table 2 Cost elements used for economical evaluation.

Category	Value	Units
Mechanical equipment price	500	$/kW
Membrane skid cost	50	$/m^2
Capital depreciation / interest charge	0.2	yr^{-1}
Power cost	0.04	$/kW
Capacity factor	85	%

Table 3 Feed specifications and membrane material separation characteristics.

Specification	Value	Units
Flue gas flow rate	298	m^3/s
Pressure	1.0	bar
Temperature	50	°C
CO_2 content	13	%
H_2O content	3.0	%
O_2 content	3.6	%
Membrane CO_2 permeance	500, 1000, 2000	GPU
CO_2/N_2 selectivity	20-200	-

5. Results and Discussion

Firstly, the mathematical model solution is checked; the two-stage vacuum design discussed by Merkel, et al. [3] was reproduced in this paper and the cost per tonne of CO_2 captured was found to be 39.3 being comparable with the value of 39 reported by [3].

5.1 Optimization Run

In this analysis, hypothetical membranes with permeances of 500, 1000 and 2000 GPU are evaluated at different selectivities of carbon dioxide relative to other gas mixture components. Only results for permeance of 1000 GPU will be discussed in this section while the other cases are shown in Fig. 4. The optimization manipulates membrane design parameters which are feed and permeate pressure of each stage, and split ratios of permeate between all possible connections shown in Fig. 3. The optimal conditions for a membrane network consisting of at most three stages with feed flow rate of 298 m^3/s are discussed below for counter-current configurations considering membrane selectivity of 50 and 100.

When membrane material selectivity for CO_2 is 50 and at the optimal design and operation of the network, the objective function value is found to be 27.7 $/tonne of CO_2 captured. The optimal configuration is found to be consisting of three stages with surface area of 0.35, 0.5 and 0.7 MMm^2, respectively. Permeate stream pressure from all stages shows optimality at minimum practical pressure which is set at 0.1 bar. The optimal split ratio of first stage permeate stream between product and recycle to feed is 1:0 and for the second stage all permeate flow is recycled to the first stage feed stream. The third stage permeate is recycled as inlet to the second stage feed stream.

The other case considered here is when membrane material selectivity is 100. At the optimal setup and operating conditions of the network, the objective function value is 26.5 $/tonne of CO_2 captured. For this scenario the optimal configuration is to have only two stages, which are the second and third stage shown in Fig. 3 with surface area of 0.5 and 1.6 MMm^2, respectively. Permeate stream pressure from the two active stages shows optimality at the minimum practical pressure which was set at 0.1 bar. Also, the optimal split ratio of first stage permeate stream between product and recycle to feed is 65:35 and for the

second active stage all permeate will be recycled and the split ratio between recycle to the second stage feed and first stage feed is 61:39.

In both scenarios, the optimal feed pressure is found at 0.91 bar. At this specific pressure, the sum of capital cost and energy consumed by mechanical equipment is at global minimum. Normally in the case of post combustion carbon capture, the feed pressure is available at atmospheric pressure (1 bar). Lowering feed stream pressure by about 0.1 bar can be done through turbo-expander to transfer feed energy in the form of pressure to permeate recycle stream.
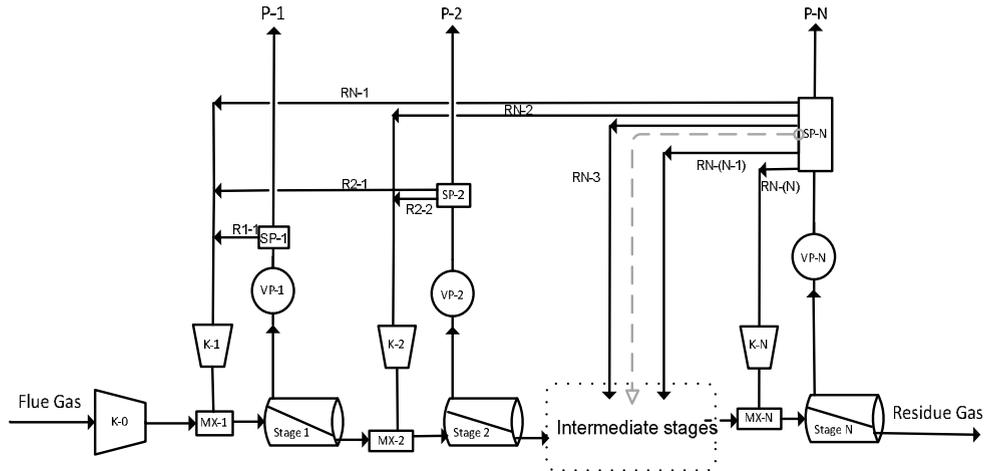

Fig. 3 Membrane superstructure network for optimization.

5.2 Membrane Optimal Selectivity

In some studies [13, 3] it has been concluded that the effect of membrane selectivity on permeate purity and recovery becomes very limited after a certain value. In order to investigate the impact of selectivity increase on cost per unit mass of CO_2 captured, the optimization case was run at different selectivities. Fig. 4 shows the cost values of membrane network at the optimal configuration corresponds to the selected selectivity. It is clear that as membrane selectivity increases the network cost per tonne of CO2 captured decreases to a certain point then the cost value starts to increase again. This specific selectivity value can be called the optimal selectivity (α_o) and it is unique depending on CO_2 permeance and network setup. When the CO_2 permeance is 1000 GPU the optimal selectivity is 144.

Even though there is optimal membrane selectivity, there is a wide range at which the objective function value is relatively stable close to the minimum. For the case when membrane permeance is 1000 GPU, the optimal selectivity is between 130 and 170.

By revisiting Fick's law, selectivity impact can be explained as follows. As the selectivity of the membrane is higher than the optimal value (α_o), the target component's stage partial pressure dramatically increases. Thus, the driving force magnitude becomes lower and therefore higher feed pressure is needed. At lower selectivity than α_o, permeate purity cannot be achieved without maximizing recycle ratio and membrane area which means higher CAPEX and OPEX.
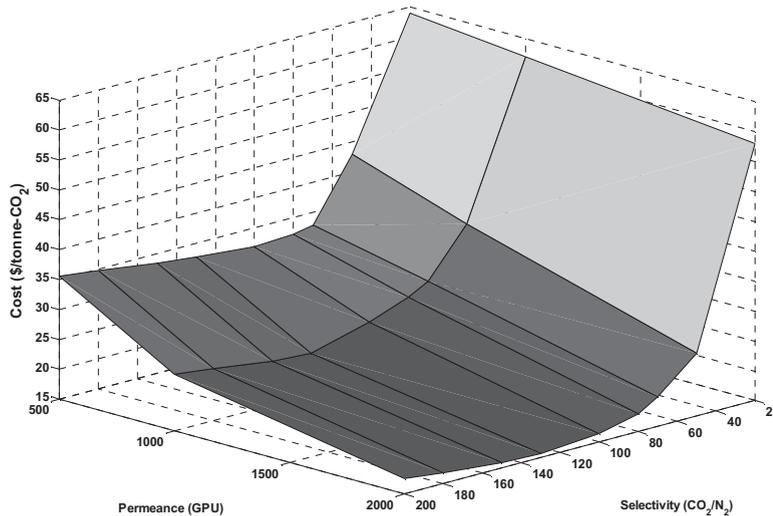
Fig.4 Dependence of objective function on membranes' selectivity and permeance.

6. Conclusion

The counter current flow mathematical model developed by Shindo et al. [11] was modified considering permeate pressure change. Then, an optimization analysis considering minimization of carbon capture cost was carried out to design a multistage membrane process. The optimization constraints were such that the recovery of carbon dioxide was more than 90% and carbon dioxide content in the permeate was higher than 90%. The optimal operating conditions in terms of feed and permeate feed pressures as well as recycle ratios were identified at different membrane's permeance and selectivity values. The optimal selectivity at which the cost per tonne of CO_2 captured was determined for different membrane's permeance. Developing membranes with higher permeance rather than the focus on obtaining highly selective membranes will eventually help membrane technology's competitiveness amongst processes for mitigation of carbon emissions. The cost of carbon dioxide can be reduced to less than $18 per tonne of CO_2 captured if a membrane with permeance higher than 2000 GPU and selectivity higher than 50 is used.

Nomenclature	
A_t	membrane total Area (m^2)
D_i	hollow fiber inner diameter (m)
D_o	hollow fiber outer diameter (m)
F	retentate flow rate (mole/s)
f	retentate normalized flow rate ($f = F/F_f$)
G	permeate flow rate (mole/s)
g	permeate normalized flow rate ($g = G/F_f$)
N	number of fibers in membrane module
P_h	feed side pressure (Pa)
P_l	permeate side pressure (Pa)
Q_m	permeability of the highest permeable component

R	ideal gas constant (m^3 Pa K^{-1} mol^{-1})
R_e	Reynolds number
S	dimensionless membrane area
T	feed temperature (°K)
x_i	feed side mole fraction of component i
y_i	permeate mole fraction of component i
α_{ji}	selectivity of component j relative to component i
γ	pressure ratio
δ	membrane thickness (m)
μ_m	gas mixture viscosity (Pa . s)
ζ	fiber wall friction factor

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