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A Theoretical Model for Cost Optimization of Multicomponent Mixtures across Membranes in a Permeation Unit

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Abstract—**The work presented here deals with a simplistic model for optimizing the total cost of a permeating gas mixture in a membrane separation process. A scheme, which is valid for any number of components, is developed taking into consideration the various fixed and operating costs encountered during the process. The outline proposed is general and can be extended to incorporate other costs specific to a particular industry as well. The minimum cost (expenditure) is then calculated with respect to the membrane area. The effect of varying the membrane area, operating conditions or the feed composition is also studied. It is expected that knowledge of the economics of the membrane separation process can lead to cheaper and more efficient processes by varying the operating conditions.**

Keywords- optimization, membrane separation, permeation, cost economics, multicomponent mixture

I. INTRODUCTION

Gas separation by selective permeation through membranes has attracted considerable attention since the 1950s particularly in the area of separation of hydrogen from refinery streams, SO_2 removal from flu gases, and separation of equilibrium products from reactants. Developments in schemes of economic optimizations of operation, (as in [1], [2]) are making permeation techniques economically competitive with respect to other separation methods like distillation. Further it is known that membrane separation processes are a good alternative compared to more established separation techniques like pressure swing adsorption and cryogenic distillation [3]. Therefore from an economic viewpoint a theoretical predictability of the cost of separation is desirable before investing large amounts into the process.

As most of these input feeds consist of more than two components, the proposed outline of such a scheme must be validated for a multi-component mixture. Majority of the simulation techniques presented in previous works ([4]) for calculating the output (permeate and retentate) compositions require the information of stage cut or membrane area beforehand. Based on this prerequisite information of membrane area (stage cut), the stage cut (membrane area) is calculated.

In this study a hypothetical model is developed to study the cost expenditure in a membrane separation process. It should be noted that increasing the membrane area increases the process cost but also increases the degree of separation and thus from an economic viewpoint, a standoff is required. As expected, this would depend on the feed composition and the operating conditions.

II. THEORY

Schematic diagrams of permeation units are explained in Fig I. A single stage is divided into two units by a non-porous membrane. Feed with molar flow rate Q_f enters from one division of the unit at a higher pressure P_h, with the mole fraction of the i^{th} component being denoted as xf_i. A fraction of the feed, Q_p is allowed to selectively permeate through a membrane, of area A and thickness d, to the other division maintained at a lower pressure P_l. The unpermeated stream (or depleted stream) exits the first division at a molar flow rate of Q_o. yp_i and xo_i denote the mole fractions of the i^{th} component of feed for the enriched and depleted division respectively. K_i denotes the permeability of the i^{th} component. Further notation is explained where it is used.

An expensive product present in the form of a mixture, along with other components, is usually of considerably lesser use than when it is in the pure form. Thus, the expensive components of the feed are desired to be separated the most and the permeating conditions should be so adjusted that a mole fraction approaching unity in the permeate or retentate stream (depending on high or low permeability, respectively, of the component) is achieved.

The below mentioned assumptions are made for the permeation process (same as in [4]):

1. The permeability of each component is the same as that of the pure species and is independent of pressure.
2. Steady state is assumed.
3. The membrane thickness is uniform.
4. The total pressure on each side of the membrane is constant.
5. In the direction perpendicular to the membrane, there are no concentration gradients.
6. Plug flow is assumed.

The following assumptions are made for developing the cost model:

1. Component separation costs follow a relation with purity of the form,

$$C_i = C_{oi}(1-x_i)/x_i \tag{1}$$

where,

C_{oi} = cost of the pure form of one mole of the i^{th} component

and,

x_i = mole fraction of the i^{th} component in the mixture.

The basis for this assumption is explained below.

2. Operating costs are constant with respect to the degree of separation.
3. There is no wear and tear of the membrane during a cycle and thus its cost does not vary in the course of a single cycle.
4. The separation is assumed to be a batch process.

A pure component requires no separation and thus its separation cost is essentially zero. Similarly, a mixture which has no quantity of a particular component requires an infinite amount of enrichment (or an infinite cost) to make it perfectly pure with respect to that component. A simplistic function obeying this relation is,

$$f(x) = (1-x)/x \tag{2}$$

because,

$$\text{as } x \to 0,\ f(x) \to \infty$$
$$\text{as } x \to 1,\ f(x) \to 0$$

Taking the variable x to be the mole fraction and C_o to be the constant of proportionality, the separation cost is as denoted in (1).

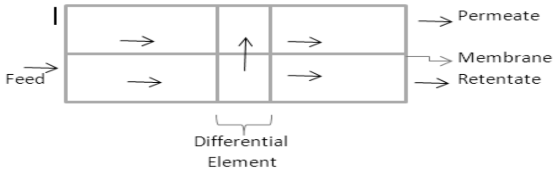

FIG I COCURRENT FLOW ACROSS MEMBRANE

The following equations directly follow from mass balances on the whole unit and on the i^{th} component respectively:

$$Q_f = Q_p + Q_o \tag{3}$$
$$Q_f\, xf_i = Q_o\, xo_i + Q_o\, yp_i \tag{4}$$

Also it follows from the convention used that,

$$\sum xf_i = 1 \tag{5}$$
$$\sum xo_i = 1 \tag{6}$$
$$\sum yp_i = 1 \tag{7}$$

Four ratios are frequently used in membrane separation literature in various forms. Here again the convention used is as followed widely in literature:

A. Stage cut

$$s = Q_p/Q_f = (Q_f - Q_o)/Q_f \tag{8}$$

B. Pressure ratio

$$Pr = P_l / P_h \tag{9}$$

Where P_l, P_h denote the pressures on the permeated and feed side respectively. h and l denote high and low respectively.

C. Area ratio

$$a = AK_1\, P_h / (d\, Q_f) \tag{10}$$

D. Ideal Separation Factor,

$$g_i = Ki/K_1 \tag{11}$$

where K_1 is the permeability of the most permeable component.

Three types of costs are dealt with here-operating costs, membrane cost and the separation costs. With each operating cycle there arise expenditures due to the maintenance of operating pressures, injection of feed, withdrawal of permeate and retentate, removal of fouling etc. The sum of these operating costs is assumed to be constant for a cycle, with the net operation cost being this sum and denoted by C'/cm^2 per cycle (in units of currency/cm^2). The cost of the membrane is C/cm^2 (in units of currency/cm^2).

Further, as developed in (1), the variable separation costs for one cycle (per unit mole) would be,

$$VC' = \sum [\{C_i (1-x_i)/x_i\} - C_i\{(1-y_i)/y_i + (1-xo_i)/xo_i\}] \tag{12}$$

$$FC' = A\,(C + C')/10^4 \tag{13}$$

where VC' and FC' are the variable cost and the fixed costs respectively in units of currency per unit mole and area is entered in units of cm^2. It can be noted that the negative of VC' is essentially the profit associated with the i^{th} component.

Hence the total variable (separation) cost associated with a cycle would be,

$$VC = \sum [n\{C_i (1-xf_i)\} - C_i\{ n'(1-y_i) + n''(1-xo_i)\}] \tag{14}$$

where n ,n' n'' are the total number of moles in the feed, permeate and retentate respectively. The values of n, n' and n'' are calculated using the ideal gas law, PV=nRT.

The total cost associated would thus be,

$$TC = FC + VC \tag{15}$$

Now we need the relation between the feed composition and the permeate side composition. Four types of flow are widely dealt with in literature- perfect mixing, cross flow, cocurrent and countercurrent flow. Due to the similarity in the cost calculation scheme (presented in this study) for all the cases and thus to avoid repetitiveness, here only the cocurrent case is handled. It is pointed out that the only difference in cost calculation for the four cases is between the equations linking the output to the input concentrations.

The cocurrent case is shown in Fig I. This has been discussed in considerable detail for multi-component mixtures ([4]) in the dimensionless form where the final form of the equations is as follows:

$$dq / da = -\sum [g_i(xo_i - Pr\, y_i)] \quad (16)$$

$$dxo_i /da = [xo_i (-dq/da) - g_i(xo_i - Pr\, y_i)] / q \quad (17)$$

where q is the dimensionless quantity obtained by dividing the flow rate at any point by the feed inflow rate as,

$$q = q_a / Qf \quad (18)$$

The boundary conditions for the n+1 equations presented above are as follows,

$$xo_i|_{a=0} = xf_i \quad (19)$$

$$q|_{a=0} = 1 \quad (20)$$

The relation between the permeate side and feed side compositions obtained from and (3), (4) and (18) is,

$$y_i= [xf_i - q\, xo_i]/ [1-q_a] \quad (21)$$

Thus knowing the values of d, P_h, K_0, g_i's and pressure ratio we can find out the values of area fraction and output concentrations. Knowing these values, the total cost can be found using (13), (14) and (15).

III. RESULTS AND DISCUSSIONS

The process conditions for the separation of a four component mixture are reproduced in Table I and Table II. The costs of pure hydrogen, oxygen and nitrogen are obtained from [6], [7] and [8]. The price of methane could not be acquired due to strong market variations in natural gas pricings. Thus the cost value of methane is arbitrarily assumed to be the mean (average) of the remaining three. The errors from this assumption are not expected to be significant as the cost values are very small as compared to the membrane costs. These values are replicated in Table III. For the operating and membrane costs, the minimum value of the range given in [10] is used. Further the replacement membrane cost, given in [10], is assumed to be the same as the original membrane cost. These values are reproduced in Table IV.

TABLE I
OPERATING PARAMETERS FOR SEPARATION OF MULTI-COMPONENT MIXTURE, (FROM [5])

P_h	380 cm Hg
P_l	50 cm Hg
d	2.54 mm
Qf	10^6 cm^3/s

TABLE II
OPERATING PARAMETERS FOR SEPARATION OF MULTICOMPONENT MIXTURES, (FROM [6])

Gas	**Permeability x10^7 (cm^3.cm/ cm^2.s.cmHg)**	**xf_i**
Hydrogen	.2	.10
Nitrogen	.11	.23
Oxygen	.044	.40
Methane	.013	.27

TABLE III
PURE STREAM COSTS CONVERTED TO COST PER UNIT MOLE (FROM [7], [8], [9])

Gas	**Cost in US \$ (in units per mole)**
Hydrogen	0.24
Nitrogen	0.112
Oxygen	0.096
Methane	0.149

TABLE IV
OPERATING AND FIXED COSTS IN US \$- TAKEN FROM [10]

Operation Cost/m^2	300
Membrane Cost/m^2	30

MATLAB codes were generated to find the VC and FC presented in (13) and (14) based on the values obtained from equations (16) - (21). The simulation yielded the results presented in Table V. It should be noted that in Table V, the variable costs are divided by 10^4 whereas the total and fixed costs are divided by 10^8 .This is done to provide greater clarity with respect to the variation patterns. The large difference in the orders of the costs must be noted.

Fig.2 shows how all the three costs-VC, FC and TC, vary with the area fraction. Again to provide greater clarity, the scale used is same as in Table V. The FC, arising primarily because of the operational costs, is the significant contributor in the total cost. This is because of the large magnitude of membrane areas. The VC also increases with increasing area fraction (stage cut) –although it remains very close to zero.

Further, the individual separation costs are analyzed. A negative value of separation cost indicates that the separation cost involved with the final mixture (permeate plus retentate) is more than that of the feed- implying that the separation has occurred 'badly'. It is seen from Fig 3 that the separation cost of component 1(which was the most expensive of the given four) always remains positive;

indicating that if extraction of hydrogen (component 1) was the required aim-it is a successful experiment. However, for the other three components, these values move from negative to positive indicating that if the main aim was to separate either of them- a particular minimum value of stage cut is desired. This minimum value is, obviously, the value at which the variable costs intersect the horizontal line y=0 in Fig 3.

It should also be noted that the VC is increasing at the expense of greater expenditure in fixed costs. It is also seen from Table V that the VC increases, although very slowly, with increasing area fraction (stage cut). This shows that in terms of individual economics this is always desired. However, the exact value of the compromise between separation and cost is to be decided by the industry depending on the purity demanded by a customer.

It is stressed that the above results provide qualitative estimates alone. However it is expected that they do provide us an accurate idea of the pattern and order of cost variation. With actual industry values and an exhaustive incorporation of operating costs a quantitative estimate of the data could be found.

TABLE V
VARIATION OF COSTS WITH AREA FRACTION AND STAGE CUT

a	**Stage Cut**	**FC x10^8**	**VC x10^4**	**TCx10^8**
0.5	0.1103	0.0543	-0.0004	0.0543
1.0	0.2120	0.1086	0.0006	0.1086
1.5	0.3055	0.1628	0.0015	0.1628
2.0	0.3912	0.2171	0.0023	0.2171
2.5	0.4697	0.2714	0.0031	0.2714
3.0	0.5414	0.3257	0.0038	0.3257

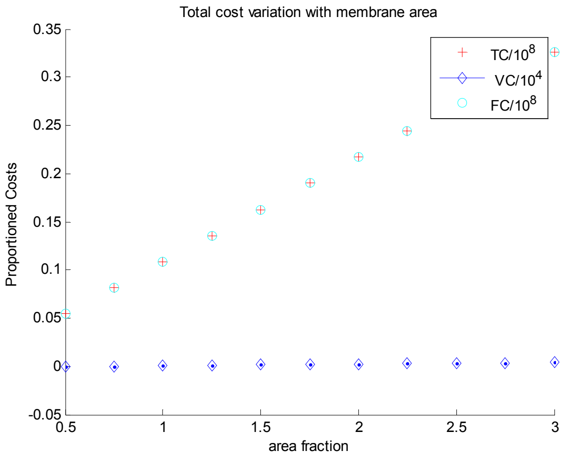

FIG 2. VARIATION OF TOTAL, VARIABLE AND FIXED COSTS WITH RESPECT TO AREA FRACTION

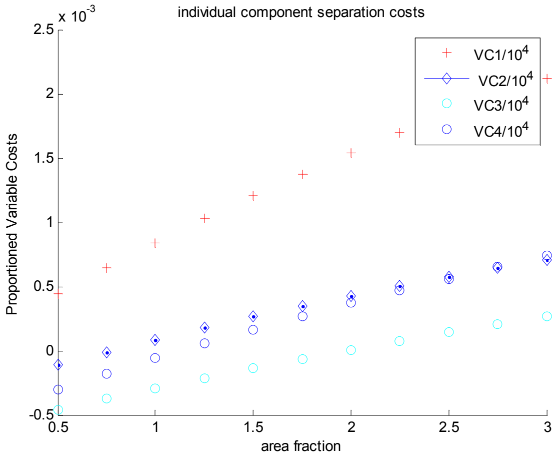

FIG 3. VARIATION OF SEPARATION COSTS OF EACH COMPONENT WITH RESPECT TO AREA FRACTION

IV. FUTURE WORK

With a precise knowledge of the cost of the operating parameters and the mixture components, a more accurate numerical model can be developed. It is again pointed out that the pattern of the variation is expected to be similar.

Further, the relationship assumed for the component cost can be replaced with a numerical correlation obtained from the industry. If a mathematical model is desired (as was in this particular study) instead of a numerical relationship, one in which standard deviations of the (overall) mixture are taken into consideration is another strong alternative.

Also the simulation can be made for a continuous process, instead of batch, taking into consideration the number of cycles required to obtain a desired degree of separation. The cycle costs could then be added to give the total operating costs.

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