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MODELLING AND SIMULATION OF RETENTATE-PERMEATE RECYCLE PREMEATOR FOR THE ENRICHMENT OF METHANE

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Abstract. The purity of less permeable component (CH_4) can be enhanced by using a retentate-permeate recycle permeator. A mathematical model has been derived and the effect of some parameters on the retentate purity and recovery have been studied through simulation. The retentate-permeate recycle permeator has been found to be more effective at low pressure ratio, low composition of the less permeable component in the feed, and large ideal selectivity. There is an optimal range of dimensionless membrane area for effective recycle. The applicability of retentate-permeate recycle permeator in enrichment of methane from biogas and natural gas has been considered. It was found that the retentate-permeate recycle permeator has the potential to be used in enrichment of methane in biogas.

Keywords: Membrane, permeator, methane enrichment, biogas, modelling, simulation

Abstrak. Ketulenan komponen kurang telap (CH_4) boleh dipertingkatkan dengan menggunakan penelap kitar semula bendalir tertelap-tertahan. Sebuah model matematik telah dibangunkan dan kesan parameter terhadap ketulenan dan pemulihan aliran sisa telah dikaji melalui penyelakuan. Penahan didapati lebih berkesan digunakan pada keadaan nisbah tekanan yang rendah, komposisi komponen kurang telap yang rendah dalam suapan, dan kememilihan unggul yang tinggi. Terdapat juga satu julat optimum bagi luas membran tak berdimensi supaya penelap kitar semula boleh beroperasi dengan berkesan. Kebolehgunaan penelap ini dalam pengayaan metana daripada biogas dan gas asli turut dipertimbangkan. Penelap kitar semula didapati berpotensi untuk digunakan dalam pengayaan metana daripada biogas.

Kata Kunci: Membran, penelap, pengayaan metana, biogas, pemodelan, penyelakuan

1.0 INTRODUCTION

Membrane-based gas separation has already been accepted as a standard unit operation in the chemical process industry [1]. As compared to the conventional gas separation technologies, such as absorption, pressure swing adsorption, and cryogenic separation, membrane processes have many advantages: modest energy requirements, modular equipment, and easy scale up. Since single stage permeator does not always give the desire degree of separation desired, a number of configurations have been

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proposed to improve the degree of separation of a membrane system. These are multimembrane permeator, recycle permeator, continuous membrane column, internally staged permeator, and permeator with permeate purging [2,3,4,5]. Most of these configurations focused on the module performance where permeate stream is the desired product.

Tsuru and Hwang [6,7] studied theoretically and experimentally a retentate-permeate recycle permeator (Figure 1). They observed that the purity of the less permeable component in the retentate stream could be enhanced using this configuration. Generally the principle behind the retentate-permeate recycle permeator is similar to the permeator with purging, except that additional purging line is not required. By recycling a small portion of the retentate stream to the permeate stream, the partial pressure of the more permeable component in the permeate stream reduced, thus enhancing the driving force of the more permeable component. Consequently, the more permeable component in the feed stream could be removed more easily than a non-recycle system, resulting in a higher purity of the less permeable component in the retentate stream.

Practical examples where retentate is the desired product include production of nitrogen from air, and enrichment of methane from biogas and natural gas. Crude natural gas contains mainly of methane with 10-20% CO_2 and some trace impurities. With the search for cleaner and more efficient fuel, upgrading of low quality natural gas which contains higher amount of CO_2, sometimes up to 70% has received much attention [8].

A related application is the upgrading of biogas, which consists of more than 50% methane, the remaining being mainly CO_2 and small amount of impurities. Both natural gas and biogas need to be purified to pipeline quality (98% methane) prior to its transport in order to minimize corrosion and to increase the heating value. Our long-term goal is to design an integrated membrane system for the production of pipeline quality natural gas and biogas.

In this paper, some parameters affecting the methane enrichment using a retentate-permeate recycle permeator were studied theoretically. The feasibility of applying the recycle permeator in enrichment of methane was considered.

2.0 MATHEMATICAL MODEL

2.1 Assumptions

The development of the mathematical model was based on the assumptions given below:

(1) The permeation process obeys Fick's Law.
(2) There is no pressure drop in the shell side and tube side of the permeators. Gorrison [9] developed a transport modulus that could be used to select

suitable fiber dimensions to minimise the effect of pressure drop in the tube side.

(3) Permeability of each gas species is the same as the pure gas, and is independent of pressure and composition.

(4) Plug flow exists in the feed and permeate streams and there is no axial mixing.

(5) Concentration polarization is negligible.

2.2 Development of the Model

Figure 1 shows schematically a retentate-permeate recycle permeator. The feed enters with a higher pressure, while the permeate leaves with a lower pressure. For a surface element dA, the overall mass balance is described by:

$$-dF = dG \tag{1}$$

or

$$-dF = dA\ \{\ Q_1\,(P_f x - P_p y) + Q_2[P_f\,(1-x) - P_p\,(1-y)\ ]\ \} \tag{2}$$

and the mass balance for the more permeable component (CO_2) is:

$$-d(\mathrm{xF}) = \mathrm{d}(\mathrm{yG}) \tag{3}$$

or

$$-d(xF) = dA\ Q_1(P_f x - P_p y) \tag{4}$$

where F is the molar flowrate on the feed (high pressure) stream; G is the flowrate on the permeate (low pressure) stream; P_f and P_p are the pressure on the feed side and the permeate side, respectively; Q is the permeation rate; x and y are the mole fraction of CO_2 on the feed side and the permeate side, respectively. The subscripts 1 and 2 refer to the more permeable component (CO_2) and the less permeable component (CH_4), respectively. Solving for dx from Equation (4) gives:

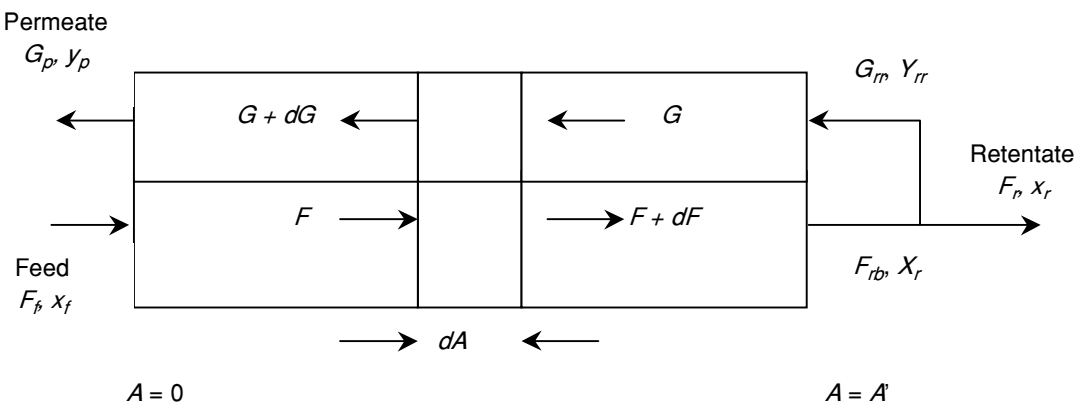

Figure 1 Schematic diagram of a retentate-permeate recycle permeator with countercurrent flow

$$\frac{dx}{dA} = -\frac{1}{F}\left[Q_1\left(P_f x - P_p y\right) + x\frac{dF}{dA}\right] \tag{5}$$

Integration of Equations (1) and (3) from an arbitrary point to the permeator's outlet yields

$$G = F - F_{rb} + G_{rr} \tag{6}$$

and

$$y = \frac{xF - x_r F_{rb} + y_{rr} G_{rr}}{F - F_{rb} + G_{rr}} \tag{7}$$

where F_{rb} and G_{rr} are the flowrate before recycle and flowrate recycled to the permeate, respectively; Y_{rr} is the mole fraction of CO_2 in the recycle stream. For retentate-permeate recycle permeator, the following relationshi ps hold:

$$Grr = RFr \tag{8}$$

$$y_{rr} = x_r \tag{9}$$

where R, the recycle ratio is defined as the fraction of retentate stream that is recycled to the permeate stream. The relationship between F_r and F_{rb} is:

$$F_r = F_{rb} / (R+1) \tag{10}$$

Substituting Equation (10) into Equation (8), yields:

$$G_{rr} = \left(\frac{R}{R+1}\right)F_{rb} \tag{11}$$

Substituting Equations (9) and (11) into Equations (6) and (7), gives:

$$G = F - \left(\frac{1}{R+1}\right)F_{rb} \tag{12}$$

$$y = \frac{xF - x_r F_{rb}\left(\frac{1}{R+1}\right)}{F - F_{rb}\left(\frac{1}{R+1}\right)} \tag{13}$$

When $R = 0$, the recycle permeator is reduced to a normal single stage permeator, and Equations (10), (12), and (13) become:

$$F_r = F_{rb} \tag{14}$$

$$G = F - F_r \tag{15}$$

$$y = \frac{xF - x_r F_r}{F - F_r} \tag{16}$$

At the closed end of the permeator, $A = A'$, Equation (16) becomes indeterminate. By applying L'Hospital rule, the following is obtained:

$$\frac{y}{1-y} = \frac{Q_1\left(P_f x - P_p y\right)}{Q_2\left[P_f\left(1-x\right) - P_p\left(1-y\right)\right]} \tag{17}$$

The following dimensionless parameters are defined:

$$S = \frac{AQ_2P_f}{F_f};\ f = F/F_f;\ g = G/F_f;\ Pr = P_f/P_p;\ \alpha = Q_1/Q_2;\ q = G_p/F_f \tag{18}$$

where S is the dimensionless membrane area; Pr is the pressure ratio; α is the ideal selectivity; θ is the stage cut, which is defined here as the ratio of permeate to feed stream (note that the usual definition of stage cut is the fraction of feed that is allowed to permeate). The governing equations in terms of dimensionless parameters are:

$$\frac{df}{dS} = \alpha\left\{\left(x - y/\mathrm{Pr}\right) + \left[\left(1-x\right) - \left(1-y\right)/\mathrm{Pr}\right]\right\} \tag{19}$$

$$\frac{dx}{dS} = -\frac{1}{f}\left[\alpha\left(x - y/\mathrm{Pr}\right) + x\frac{df}{dS}\right] \tag{20}$$

$$f_r = f_{rb}\left(R+1\right) \tag{21}$$

$$g = f - f_{rb}\left(\frac{1}{R+1}\right) \tag{22}$$

$$y = \frac{xf - x_r f_{rb}\left(\frac{1}{R+1}\right)}{f - f_{rb}\left(\frac{1}{R+1}\right)};\ g \neq 0 \tag{23}$$

When R = 0, the permeate mole fraction at the closed end is obtained by solving Equation (17):

$$y = \frac{1+(\alpha-1)\left(1/\mathrm{Pr}+x_f\right)-\sqrt{\left[1+(\alpha-1)\left(1/\mathrm{Pr}+x_f\right)\right]^2-4(\alpha-1)\alpha x_f/\mathrm{Pr}}}{2(\alpha-1)/\mathrm{Pr}} \tag{24}$$

2.3 Solution Strategy

The mathematical model developed in this study is a boundary value problem involves coupled non-linear ordinary differential equations. Analytical solutions cannot be found; therefore numerical technique is used to solve the mathematical model.

Figure 2 shows a flowchart for the solution procedure. The integration is carried out backward iteratively from $S = S'$ to $S = 0$ with an initial guess of retentate compositions, x_r and stage cut, θ until x and f at $S = 0$ obtained numerically are sufficient close to x_f and 1, respectively. Equations (19) and (20) are solved using a simple Euler method.

3.0 SIMULATION RESULTS

Typical values for CO_2-CH_4 system: $x_f = 0.7$, $\alpha = 20$, and $S = 0.1$ are used as base case conditions to illustrate the effect of some parameters on the performance of a retentate-permeate recycle permeator. Bhide and Stern [10] suggested the usage of an ideal selectivity of about 20 for cellulose acetate membrane, to account for the effect of moisture and plasticization.

3.1 Recycle Ratio

Figure 3 shows the effect of recycle ratio (R) on product purity for different pressure ratio. The mole fraction of CH_4 in the retentate stream increases with the recycle ratio. When a part of the retentate, in which the concentration of CO_2 is lower than that of the permeate, is introduced to the permeate stream, the driving force for CO_2 between the feed and permeate stream is enhanced. Consequently, more CO_2 permeates to the permeate stream, leaving behind a purer CH_4 in the retentate stream. For example, the mole fraction of CH_4 at Pr = 5 starts from 0.76 without recycle (at $R = 0$), and increases with recycle ratio before reaching an asymptotic value of about 0.88. The same effect is also seen at Pr = 10 and 30. The recycle ratio has a more pronounced effect at a smaller pressure ratio. On the other hand, the mole fraction of CO_2 in the permeate decreases gradually with recycle ratio since the permeate stream is diluted by the retentate recycle. The pressure ratio does not make a significant difference over the whole range of the recycle ratio. The retentate recycle is effective

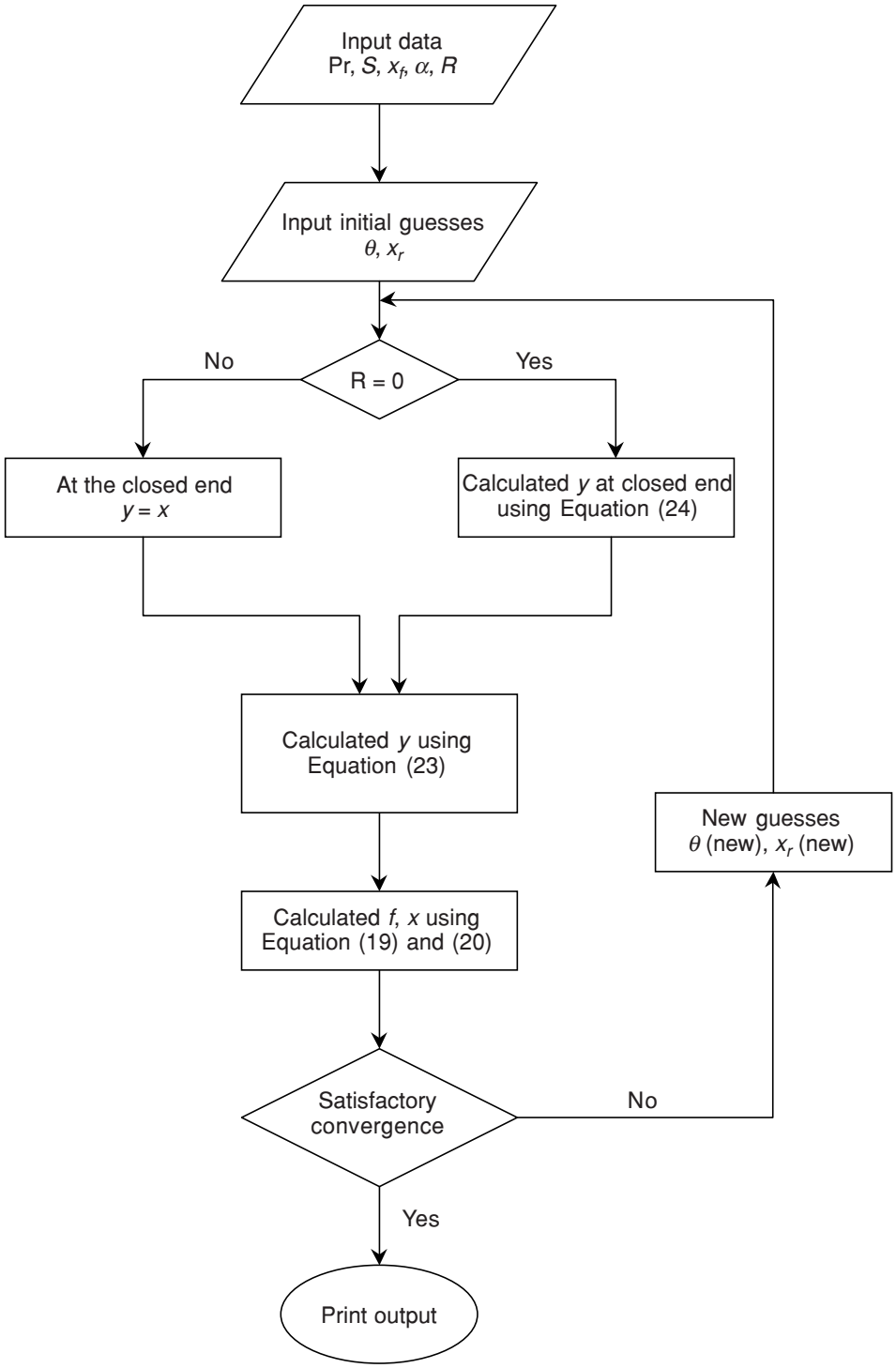

Figure 2 Flowchart for solution procedure

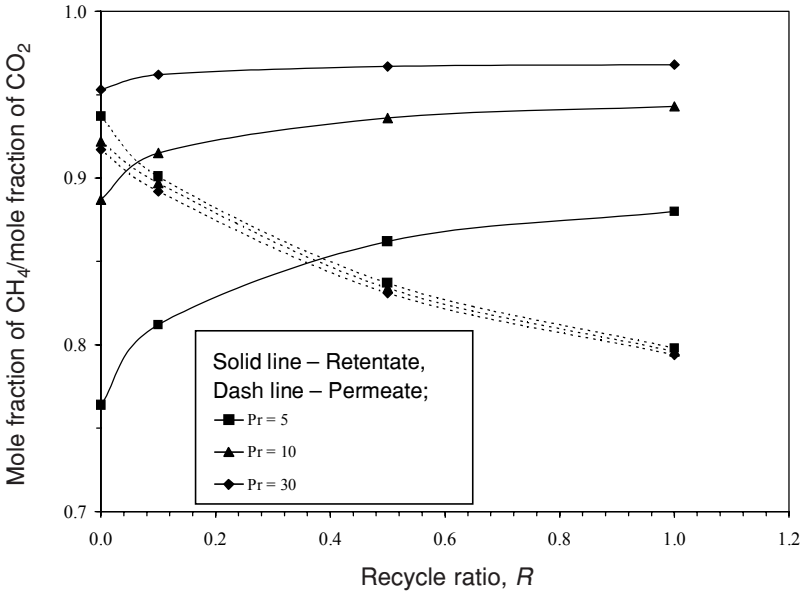

Figure 3 Mole fraction of CH_4 in retentate and mole fraction of CO_2 in permeate as a function of recycle ratio for different pressure ratio; $\alpha = 20$, $S = 0.1$, $x_f = 0.7$

for obtaining high purity of the less permeable component but may not be suitable for achieving high purity of the more permeable component.

Figure 4 shows the recovery of CH_4 in the retentate as a function of the recycle ratio. As expected, the recovery of CH_4 in the retentate decreases as the recycle ratio increase. This is because part of the retentate is recycled to the permeate.

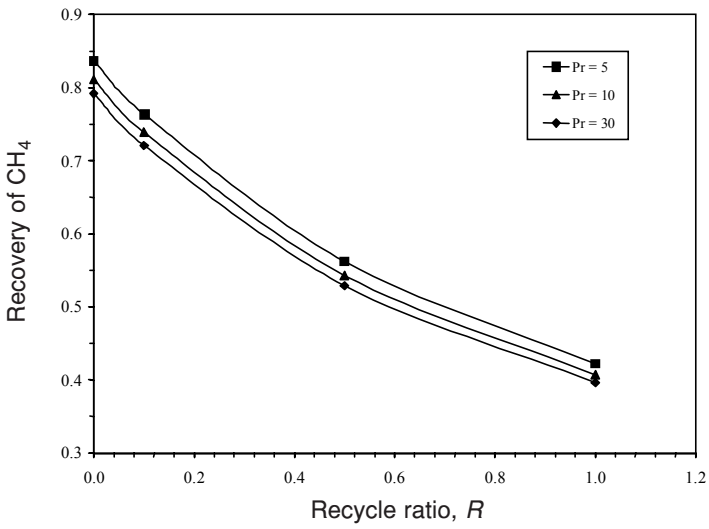

Figure 4 Recovery of CH_4 in retentate as a function of recycle ratio for different pressure ratio; $S = 0.1$, $\alpha = 20$, $x_f = 0.7$

3.2 Stage Cut

Figure 5 shows the effect of stage cut on retentate purity. Increase of recycle ratio always causes an increase in stage cut and retentate purity. For example, at $Pr = 5$, the mole fraction increases from 0.76 at $R = 0$ to 0.88 at $R = 1$. Again it appears that the recycle is more effective for a small pressure ratio than a large pressure ratio as discussed earlier. It should be noted that when retentate is the desired product, lower stage cut and higher purity are desired. However, there is a trade-off between retentate purity and recovery. As the recycle ratio increases, inevitably more CH_4 is lost to the permeate stream. In other words, CH_4 purity is increased at the expense of its recovery.

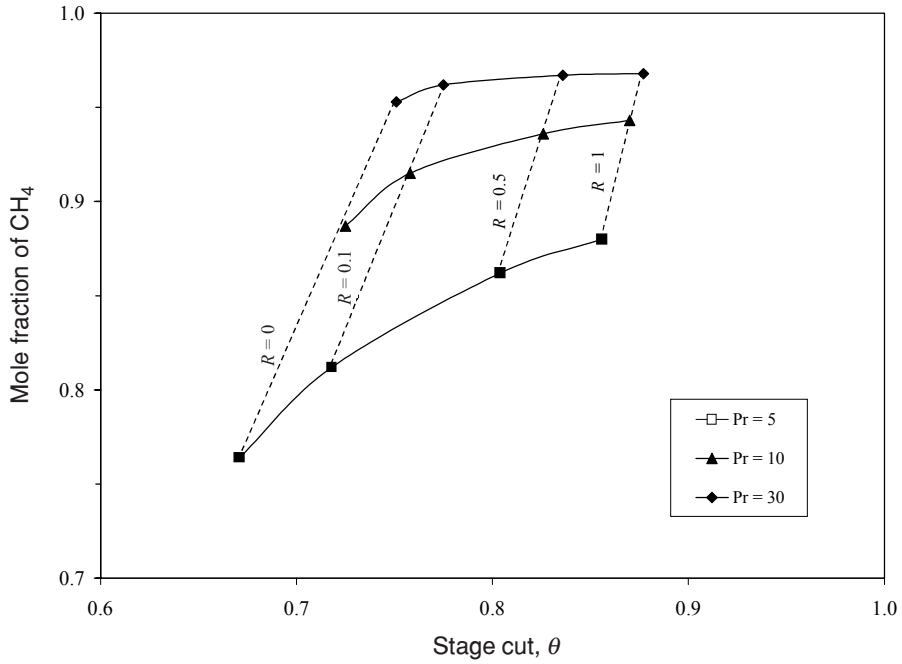

Figure 5 Mole fraction of CH_4 in retentate as a function of stage cut for different pressure ratio; $S = 0.1$, $\alpha = 20$, $x_f = 0.7$

3.3 Dimensionless Membrane Area

Figure 6 shows the mole fraction of CH_4 in the retentate as a function of dimensionless membrane area (S). For constrant α, Pr, and x_f, increasing the dimensionless membrane area means either increasing the membrane area or decreasing the feed flow rate. Increasing S increases the CH_4 purity for any value of the recycle ratio. It appears that there is an optimal range of dimensionless membrane area for effective recycle. At small dimensionless membrane area, the increase of retentate purity with recycle ratio is minimal as the permeator does not have enough membrane area to take ad-

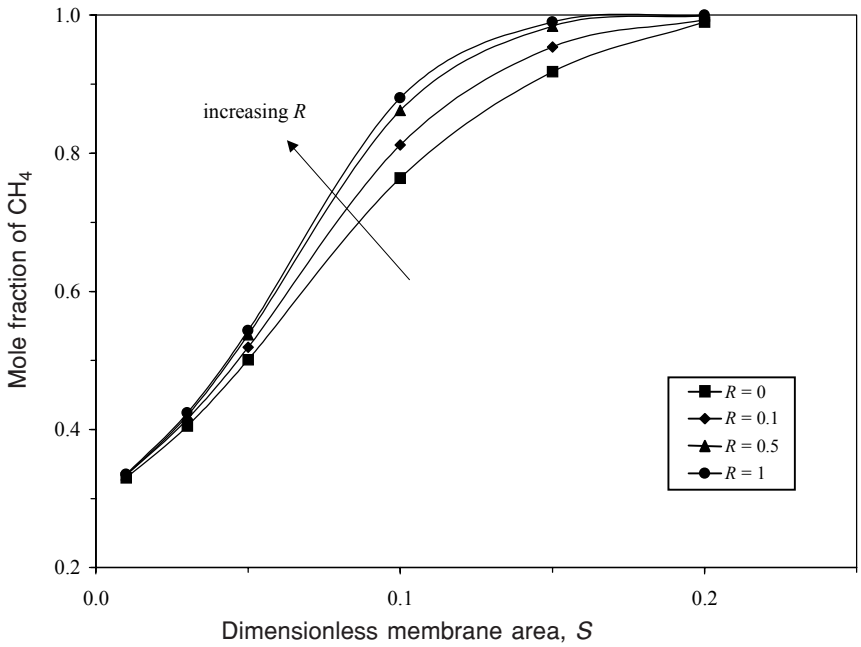

Figure 6 Mole fraction of CH_4 in retentate as a function of dimensionless area for different recycle ratio; $\alpha = 20$, $x_f = 0.7$, $Pr = 5$

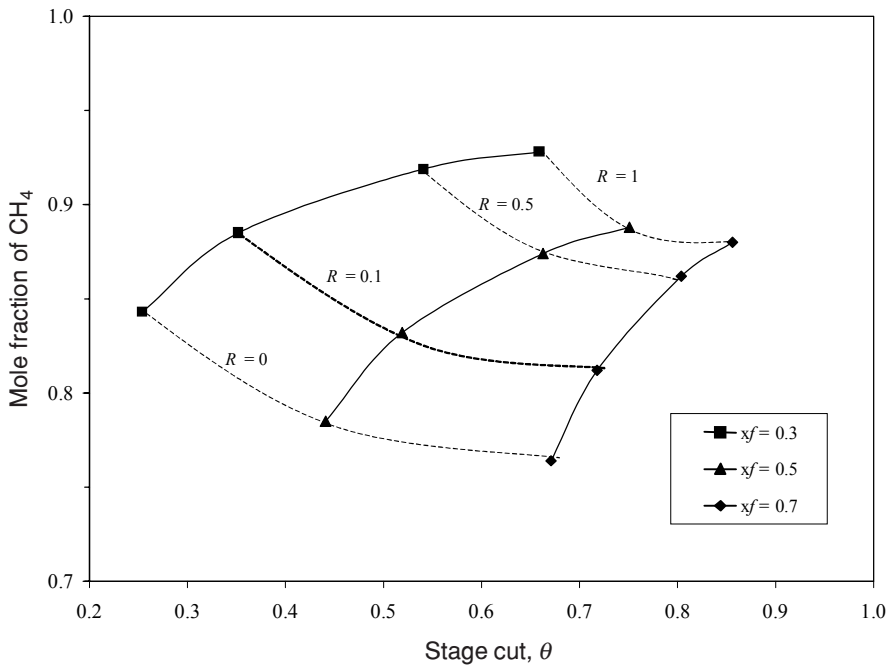

Figure 7 Mole fraction of CH_4 in retentate as a function of stage cut for different feed composition; $S = 0.1$, $\alpha = 20$, $Pr = 5$

vantage of the enhancement of driving force. On the other hand, at larger S, the flowrate of the retentate is small (since the stage cut is large), thus even a larger recycle ratio does not enhance the driving force of the more permeable component. Moreover, the CH_4 purity in the retentate without recycle is already high, thus it is difficult to achieve any significant improvement even with larger recycle ratio.

3.4 Feed Composition

Figure 7 shows the mole fraction of CH_4 in the retentate as a function of stage cut for different feed composition. As expected, similar trends are observed for all three feed compositions. The recycle is more effective at higher feed mole fraction of CO_2 as the increase of CH_4 purity is accompanied by a smaller increase of stage cut. So the retentate-permeate recycle permeator is best employed for feed with low mole fraction of CH_4.

3.5 Ideal Selectivity

Figure 8 shows the mole fraction of CH_4 in the retentate as a function of stage cut with ideal selectivity as a variable. For membrane with small ideal selectivity ($a = 10$), only marginal improvement in CH_4 purity is achieved. The retentate-permeate recycle permeator is more attractive for membrane with large ideal selectivity as the loss in productivity is compensated by the increase in purity.

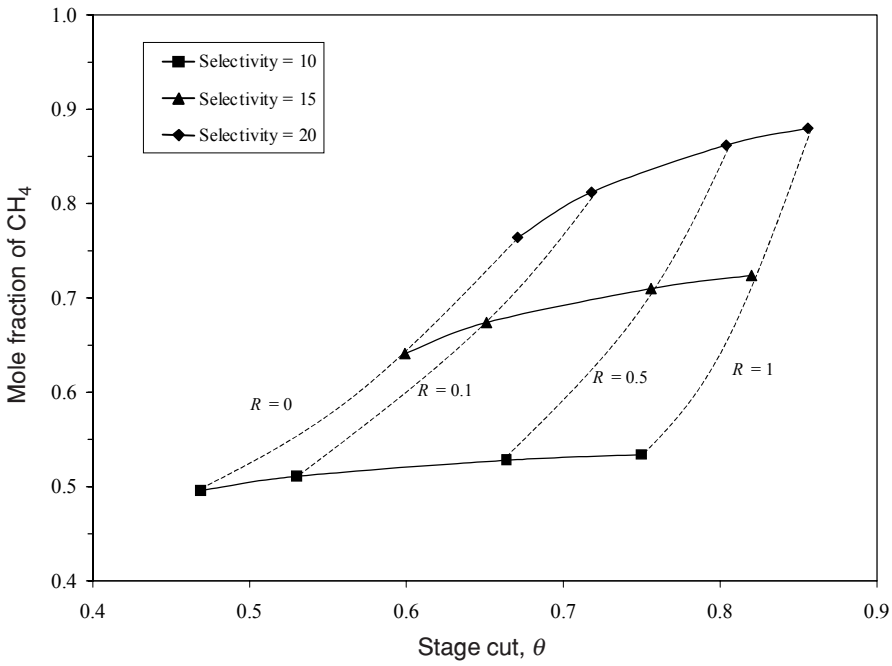

Figure 8 Mole fraction of CH_4 in retentate as a function of stage cut for different ideal selectivity; $S = 0.1$, $x_f = 0.7$, Pr=5

3.6 Applicability of Retentate-Permeate Recycle Permeator in the Enrichment of Methane

Purification of natural gas using membrane always takes advantage of the high pressure (in the range of 50 atm) of natural gas obtained at source [11]. Since the retentate-permeate recycle permeator is not effective at high pressure ratio, it is not attractive to be used in the purification of natural gas. On the other hand, it has the potential in the enrichment of methane in biogas or landfill gas. The biogas obtained needs to be compressed for permeation. A process described by Rautenbach and Welsch [12] involved a compression of up to 30 atm. By employing the retentate-permeate recycle permeator, the compression cost may be reduced. However, since retentate-permeate recycle permeator gives higher loss of methane, for practical application, further studies based on economic consideration are required. The retentate-permeate recycle permeator will become more attractive if membranes with higher selectivity than cellulose acetate are employed [13,14].

4.0 CONCLUSION

A mathematical model for retentate-permeate recycle permeator has been developed. A retentate-permeate recycle permeator is found to be effective in enhancing the purity of the less permeable component. However, the purity is gained at the expense of recovery. The retentate-permeate recycle permeator is best to be operated at low pressure ratio, low feed mole fraction of the less permeable component, and high ideal selectivity. Proper selection of membrane area and feed flowrate is essential. The retentate-permeate recycle permeator has the potential to be used in enrichment of methane from biogas. However, for practical application, detail economic evaluation is required. Future studies will include the development of a rigorous model that takes into account the effect of plasticisation, Joule-Thompson effect, mixed gas permeabilities, non-ideal gas behaviour, concentration polarisation, axial dispersion, and pressure drop in the permeator. This model could be used in the design and optimisation of membrane-based gas separation system.

REFERENCES

[1] Koros, W. J., and G. K. Fleming. 1993. Membrane-based gas separation. *J. Membrane Sci.*, 83, 1-80.

[2] Purnomo, I. S. K., and E. Alpay. 2000. Membrane column optimisation for the bulk separation of air. *Chem. Engng Sci.*, 55, 3599 – 3610.

[3] Kao, Y. K., M. M. Qiu, and S. T. Hwang. 1989. Economic evaluation of gas membrane separator designs. *Ind. Eng. Chem. Res.*, 28, 1670.

[4] Li, K., D. R. Acharya, and R. Hughes. 1990. Membrane gas separation with permeate purging. *Gas Sep. Purif.*, 4, 81 – 86.

[5] Li, K., D. Wang, D. Li, and W. K. Teo. 1998. Internally staged permeator prepared from annular hollow fibers for gas separation. *A.I.Ch.E. Journal.* 44(4): 849 – 858.

[6] Tsuru, T., and S. T. Hwang. 1994. Evaluation of retentate recycle effect on enrichment of less permeable gas component in a membrane permeator. *J. Membrane Sci.*, 94, 213 – 224.

[7] Tsuru, T., and S. T. Hwang. 1995. Permeators and continuous membrane columns with retentate recycle. *J. Membrane Sci.*, 98, 57 – 67.
[8] Stern, S. A. 1994. Polymers for gas separation: the next decade, *J. Membrane Sci.*, 94, 1 – 65.
[9] Gorissen, H. 1989. Studies on transport phenomena in hollow fibre membranes by menas of dimensionless groups, in Cecille, L. and Toussaint, J. C. (Ed.). *Future indsustrial prospects of membrane processes*. Elsevier Applied Science, 87 – 97.
[10] Bhide, B. D., and S. A. Stern. 1993. Membrane processes for the removal of acid gases form natural gas. I. process configurations and optimization of operating conditions, *J. Membrane Sci.*, 81, 209 – 237.
[11] Laverty, B., and G. O'Hair. 1990. The applications of membrane technology in the natural gas industry, in Howell, J.A. (Ed.). *The membrane alternative – energy implications for industry*. Elsevier Applied Science, 87 – 97.
[12] Rautenbach, K., and K. Welsch. 1994. Treatment of Landfill Gas by Gas-permeation – Pilot Plant Results and Comparison to Alternative, *J. Membrane Sci.*, 87, 107 – 118.
[13] Ismail, A. F., and S. J. Shilton. 1998. Polysulfone gas separation hollow fiber membranes with enhanced selectivity, *Journal of Membrane Science*, 139, 285 – 286.
[14] Baker, R. 2001. Future directions of membrane gas-separation technology, *Membrane Technology*, Issue 138, October 2001, 5 – 10.

NOMENCLATURE

A	membrane area (m^2)
S	dimensionless membrane area
F	flow rate on the feed stream (mol/s)
f	dimensionless flow rate on the feed stream
G	Flow rate on the permeate stream (mol/s)
g	dimensionless flow rate on the permeate stream
P	pressure (Pa)
Q	permeation rate ($mol/s.m^2.Pa$)
x	mole fraction of CO_2 on the feed stream
y	mole fraction of CO_2 on the permeate stream
Pr	pressure ratio
R	recycle ratio

Greek

q	stage cut
a	ideal selectivity

Subscript

f	feed stream at the inlet
r	retentate stream
p	permeate stream at the outlet
rr	recycle stream
rb	retentate flow rate before recycle
1	more permeable component, CO_2
2	less permeable component, CH_4