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LIQUID MEMBRANE PURIFICATION OF BIOGAS

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LIQUID MEMBRANE PURIFICATION OF BIOGAS

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CONTENTS

<u>Section</u>	<u>Page</u>
EXECUTIVE SUMMARY	S-1
1 INTRODUCTION	1-1
2 MODELING AND SIMULATION	2-1
Analysis of Gas Mixture Separation in a HFCLM Permeator	
Sweep Gas Mode of Operation	2-2
Conventional or Vacuum Mode of Operation	2-7
Sweep Water Mode of Operation	2-10
Determination of Effective Membrane Thickness in a HFCLM Permeator	2-15
Determination of Permeability of Nonreactive Species through an Aqueous Solution of DEA	2-15
Analysis of Facilitated Transport of CO ₂ through an Aqueous Solution of DEA	2-16
Simulation Techniques for Separation Problems in HFCLM Permeator	2-20
Solution Procedure for Facilitated Transport Analysis	2-21
Generalized Two Dimensional Model for Membrane Thickness Determination	2-21
3 EXPERIMENTAL	3-1
Determination of Wettability, Bubble Points and Break-through Points	3-1
Fabrication of Small Scale HFCLM Permeators	3-2
Fabrication of Large Scale HFCLM Permeators	3-10
Permeator Testing Under Static Pressure	3-15
Description of Purification Loop for Various Modes in Small Scale Operation	3-17
Sweep Gas Mode	3-17
Conventional Polymeric Membrane Mode	3-22

Vacuum Mode	3-22
Sweep Water Mode	3-25
Description of the Larger Purification Loop	3-25
Experimental Procedure	3-29
Measurement of Gas Permeability through the Liquid Membrane	3-32
Calibration and Analysis	3-35
4 RESULTS AND DISCUSSION	
Estimation of Pure Component Gas Permeabilities through Water	4-1
Estimation of Pure Component Gas Permeabilities through Aqueous Solutions of DEA	4-1
Estimation of Effective Membrane Thickness in Small Permeators	4-10
Purification Studies of Model Biogas Mixtures in Sweep Gas Mode through Different Liquid Membranes in Small Scale Operation	4-19
Water as Liquid Membrane and 40% CO ₂ - 60% N ₂ as Feed Gas	4-22
Water as Liquid Membrane and 40% CO ₂ - 60% CH ₄ as Feed Gas	4-27
30 wt% K ₂ CO ₃ Solution as Liquid Membrane and 40% CO ₂ - 60% N ₂ as Feed Gas	4-34
Aqueous Solution of DEA as Liquid Membrane and 40% CO ₂ - 60% N ₂ as Feed Gas	4-41
Aqueous Solution of 20 wt% DEA as Liquid Membrane and 40% CO ₂ - 60% CH ₄ as Feed Gas	4-56
Aqueous Solution of 10 wt% DEA as Liquid Membrane and 5% CO ₂ - 95% N ₂ as Feed Gas	4-60
Aqueous Solution of NMP as Liquid Membrane and 40% CO ₂ - 60% N ₂ as Feed Gas	4-60
Purification Studies of Model Biogas Mixtures in Conventional Polymeric Membrane Mode with Different Liquid Membranes	4-68
Water as Liquid Membrane and 40% CO ₂ - 60% N ₂ as Feed Gas	4-68

	30 wt% K_2CO_3 Solution as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas	4-74
	Purification Studies of Model Biogas Mixtures under Vacuum Mode of Operation	4-80
	Water as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas	4-80
	Water as Liquid Membrane and 40% CO_2 - 60% CH_4 as Feed Gas	4-97
	7 wt% K_2CO_3 Solution as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas	4-103
	Purification Studies of Model Biogas Mixtures in Sweep Water Mode through Different Liquid Membranes	4-103
	Water as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas	4-103
	Water as Liquid Membrane and 40% CO_2 - 60% CH_4 as Feed Gas	4-112
	30 wt% K_2CO_3 Solution as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas	4-118
	30 wt% K_2CO_3 Solution as Liquid Membrane and 40% CO_2 - 60% CH_4 as Feed Gas	4-118
	20 wt% DEA Solution as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas	4-118
	Estimation of Effective Membrane Thickness in Large Permeators	4-125
	Purification Studies of Model Biogas Mixtures in Large Scale Operation	4-129
	Water as Liquid Membrane and CO_2 - N_2 Gas Mixture as Feed	4-129
	20 wt% DEA Solution as Liquid Membrane and CO_2 - N_2 Gas Mixture as Feed	4-131
	20 wt% DEA Solution as Liquid Membrane and CO_2 - CH_4 Gas Mixture as Feed	4-144
	Best Performances under Different Modes of Operation	4-151
5	PRELIMINARY ECONOMIC ANALYSIS	5-1
6	INTERACTIONS WITH CORPORATIONS REGARDING HFCLM TECHNOLOGY	6-1
7	NOMENCLATURE	7-1
8	REFERENCES	8-1

EXECUTIVE SUMMARY

Conventional gas purification technologies are highly energy intensive. They are not suitable for economic removal of CO_2 from methane obtained in biogas due to the small scale of gas production. Membrane separation techniques on the other hand are ideally suited for low gas production rate applications due to their modular nature. Polymeric membranes as well as liquid membranes have been investigated earlier for biogas purification. Polymeric membranes suffer, in general, from low values of selectivities and permeabilities. Although liquid membranes possess a high species permeability and selectivity, they have not been used for industrial applications due to the problems of membrane stability, membrane flooding and poor operational flexibility, etc. A new hollow-fiber-contained liquid membrane (HFCLM) technique has been developed recently. This technique overcomes the shortcomings of the traditional immobilized liquid membrane technology.

The new technique uses two sets of hydrophobic, microporous hollow fine fibers, packed tightly in a permeator shell. The inter-fiber space is filled with an aqueous liquid acting as the membrane. The feed gas mixture is separated by selective permeation of a species through the liquid from one fiber set to the other. The second fiber set carries a sweep stream, gas or liquid, or simply the permeated gas stream.

The objectives of the present investigation were as follows.

1. To study the selective removal of CO_2 from a model biogas mixture containing 40% CO_2 (the rest being N_2 or CH_4) using a HFCLM permeator under various operating modes that include sweep gas, sweep liquid, vacuum and conventional permeation.
2. To develop a mathematical model for each mode of operation.
3. To build a large-scale purification loop and large-scale permeators for model biogas separation and to show stable performance over a period of one month.

Extensive purification studies with a model 40% CO_2 - 60% N_2 feed mixture demonstrated excellent purification capabilities of HFCLM permeator under various operating modes. Sweep gas mode of operation with 20 wt% DEA as a

liquid membrane yielded a purified gas stream containing only 6% CO_2 with a N_2 recovery of 95%. The amount of sweep helium gas permeation into the product stream was very low, suggesting that air might be used as a sweep gas in a commercial application. The permeability of N_2 or O_2 being lower than that of helium, the contamination of the product stream (especially with respect to O_2) would be very low. Sweep water mode of testing was able to recover 98% of the feed nitrogen with a product purity of 90% N_2 . In both conventional permeation and vacuum modes of operation, a purified gas stream containing only about 5% CO_2 was observed. The N_2 recoveries were about 72% and 83%, respectively. In the last three cases, pure water was utilized as a liquid membrane; thus feed gas humidification was avoided completely. Many experiments with a 40% CO_2 - 60% CH_4 feed mixture have provided similar performances.

Mathematical models have been developed for each mode of operation. The results obtained from these models describe the permeator behavior quite well. In addition, a generalized model has been developed which determines the effective liquid membrane thickness in a HFCLM permeator by solving the diffusion equation in two dimensions.

A purification loop was built for large-scale operation which provided feed gas and sweep gas to the permeator at any humidity between 0-100%. Long-term experiments with pure water and 20 wt% DEA solution as membranes and either 40 - 60 CO_2 - N_2 or CO_2 - CH_4 gas mixture as feed, demonstrated that the hollow-fiber-contained liquid membrane system can be used efficiently to separate gas mixtures with minimum maintenance over a prolonged period of time. In an industrial operation, a slow circulation of the liquid membrane with some arrangement for replenishing the liquid loss due to evaporation in the gas stream is desirable. It might eliminate the need for humidifying the gas streams completely. Moreover, the same arrangement might be used for in-situ replacement of the membrane if poisoned or contaminated by some unwanted constituents in the gas mixture.

The HFCLM technique has overcome the deficiencies of traditional liquid membrane systems by providing stable operation. Purification of biogas can be achieved to yield pipeline quality gas with high methane recovery. It is strongly recommended that the potential of this new technique be explored for

other gas treating applications such as treatment of fuel gas available from biomass and/or coal gasification, removal of CO_2 from a gas stream in denitrification bioreactor, removal of SO_2/NO_x from flue gas, natural gas processing, separation of higher olefins from hydrocarbons such as ethylene/ethane gas mixture, synthesis gas purification, oxygen enrichment of air, chlorine/hydrochloric acid gas separation from vent gases etc. Additionally, use of HFCLM modules as pre-treatment facilities for bulk purification before gas absorption towers for removing H_2S is expected to reduce the load and size of the towers drastically.

Section 1

INTRODUCTION

Conventional gas purification technologies are not suitable for economic removal of carbon dioxide from methane obtained in biogas due to the small scale of production. Membrane-based separation techniques are suited for such processes. Liquid membranes are attractive in general since they possess high species permeability and selectivity. However, the traditional immobilized liquid membrane (ILM) technique suffers from the problems of membrane stability, membrane flooding and a costly configuration. A new liquid membrane technique which bypasses the shortcomings of ILM was developed under the joint sponsorship of NYSERDA, NYGAS and GRI since 1984. The new hollow-fiber-contained liquid membrane (HFCLM) technique utilizes two sets of hydrophobic, microporous hollow fibers. The feed gas mixture is separated by preferential permeation of a gas species from one set of fibers to the other, through thin layers of liquids contained on the outside of the two sets of fibers. The fibers are packed together tightly in a shell. An account of this technique and its application to the purification of a landfill gas mixture using a sweep gas stream is available in NYSERDA Report 87-10. The current phase of the project was undertaken to investigate experimentally the short-term and long-term performances of the HFCLM permeation process for biogas purification using three different separation modes of sweep, vacuum and conventional permeation and development of mathematical models to predict the system performance under these modes of operation. The current phase of the project is also concerned with an experimental study of the continuous separation performance of a larger permeator containing 5000 fibers over periods one-month-long using the optimum mode of permeator operation. The overall task and task components are available in Table 1-1.

In the first phase of the project, the separation of model biogas mixtures has been studied using four different permeation modes. The first mode uses a sweep gas through the permeate fibers to create the proper partial pressure driving force. The second mode uses a sweep liquid e.g., water to achieve the same end. The third mode explores liquid membrane operation as if the liquid membrane were a polymeric membrane in a conventional permeator. The fourth mode uses a

TABLE 1-1

PROJECT TASKS: MASTER CHART AND SCHEDULE

PHASE I	OVERALL TASKS	TASK COMPONENTS	TARGET COMPLETION DATE
A. Explore feasibility of HFCLM separation in vacuum mode and in polymer-membrane mode of 40% CO ₂ -60% N ₂ and 40% CO ₂ -60% CH ₄ mixtures with short-term and longer-term runs in small permeators.		A.1 Procure vacuum pumps, traps, gages, CH ₄ leak detectors and alarms	12/1/86
		A.2 Investigate feasibility of purification of 40% CO ₂ -60% N ₂ in various modes with short 24-48 hr. and longer-term 48-100 hr. runs.	2/15/87
		A.3 Measure CH ₄ permeability coefficients through salt solutions and other liquid membranes immobilized in small hydrophobic films.	2/28/87
B. Develop simulation models of various modes of operation, demonstrate and select the optimum mode in small permeator.		A.4 Investigate purification of 40% CO ₂ -60% CH ₄ with various modes in short-term (24-48 hr) runs to CO ₂ level less than 5%.	4/15/87
		A.5 Achieve purification of 40% CO ₂ -60% CH ₄ to $\geq 95\%$ CH ₄ for 48-100-hour periods	5/15/87
		B.1 Develop numerical models for various modes of operation.	6/30/87
C. Design permeator and purification loop based on the optimum for larger-scale Operation		B.2 Demonstrate and select optimum mode for purified gas with $\geq 95\%$ CH ₄	8/15/87
		C.1 Design larger-scale permeator	8/31/87
		C.2 Design larger purification loop and order equipment based on A, B & C.1.	9/30/87
		C.3 Project evaluation meeting	10/1/87
		C.4 Interim report on Task A,B,C	10/1/87

PHASE II

TABLE 1-1 (Cont.)

OVERALL TASKS	TASK COMPONENTS	TARGET COMPLETION DATE
D. Fabricate and test a larger-scale permeator and a purification loop for landfill gas of CO ₂ and N ₂ , and CO ₂ and CH ₄	D.1 Set up a larger-scale purification loop	6/30/88
	D.2 Fabricate one to two large-scale permeators containing up to 500 fibers.	6/30/88
	D.3 Conduct preliminary tests of loop and permeator of D.1 and D.2	7/31/88
E. Conduct life studies for model landfill gas in the larger-scale apparatus.	E.1 Carry out trial runs lasting between 5 to 10 days for purification of 60% N ₂ -40% CO ₂ and 60% CH ₄ -40% CO ₂ mixtures	9/30/88
	E.2 Conduct one-month life test on a 60% N ₂ -40% CO ₂ mixtures	12/30/88
F. Verify numerical model for larger scale of operation		1/31/89
G. Final report preparation		2/28/89
H. Educate corporate concerns as to the benefits of this technology for their applications	H.1 Identify possible corporate sponsors	7/31/88
	H.2 Prepare descriptive documents to distribute to firms identified in Task H.1	7/31/88
	H.3 Arrange review meetings which identified firms to evaluate the technology and to determine commercial applications	12/31/88

vacuum on the permeate side to create a partial pressure difference. The separation schemes are shown in Figure 1-1.

Experimental investigations of gas separation in small HFCLM permeators for short and extended separation runs in various modes were made mainly with a feed gas mixture consisting 40% CO_2 and 60% N_2 . For sweep gas mode of operation, helium was primarily used as a sweep gas. Quite a few experiments were carried out with 40% CO_2 - 60% CH_4 gas mixture as feed and N_2 as the sweep gas. Feed pressure was generally maintained at 45 psig. The liquid membranes investigated include water, aqueous K_2CO_3 solutions (7 wt% or 30 wt%), aqueous solutions of 1-methyl-2-pyrrolidinone (NMP) (70 and 80 vol%) and aqueous diethanolamine (DEA) solutions (10, 20 and 30 wt%). Most experiments were done at 25°C.

A number of hollow-fiber-contained liquid membrane permeators were developed specifically for the project. Sometimes these permeators were used in series configurations. Continuous experimental runs have been carried out on numerous occasions for periods as long as 100 hours to determine the operational stability of this new technique. The membrane liquid pressure was around 50 psig for 45 psig feed pressure.

The operational data of these and previously available permeators in the new modes have been compared with the numerical simulation results of mathematical models developed for each mode. Species permeability information was experimentally developed separately through a few membranes to this end. Using the observed separation results and numerical simulations, a preliminary economic comparison of the various modes of operation of HFCLM permeators has been carried out.

In the second part of the project, a larger-scale purification loop was designed and constructed. Using numerical models, a permeator was also designed for larger-scale operation. Three large permeators, each containing 7000 microporous polypropylene hollow fibers, were fabricated for the project. Long-term purification runs were carried out with both CO_2 - N_2 and CO_2 - CH_4 feed mixtures for periods as long as 240 hours. The liquid membranes utilized were pure water and aqueous 20 wt% DEA solution, respectively. A one-month-long

FIGURE 1-1
FOUR SEPARATION SCHEMES FOR PURIFICATION OF BIOGAS
USING THE HFCLM PERMEATION TECHNIQUE: SCHEMATICS

life test was also conducted using a feed gas mixture containing CO_2 and N_2 and an aqueous 20 wt% DEA solution as a liquid membrane. The membrane thickness in each large permeator was determined utilizing the mathematical models developed earlier.

Section 2

MODELING AND SIMULATION

The modeling aspects of gas mixture separation in hollow-fiber-contained liquid membrane (HFCLM) permeators under various modes of operation are considered in this section. The following assumptions are used to analyze the gas permeation and separation of a binary feed gas mixture in a HFCLM permeator under various modes of operation:

1. The permeability coefficient of each nonreacting gas component through water as well as aqueous solution of DEA is same as that of the pure gas, and is independent of gas pressure.
2. There exists an effective liquid membrane thickness, d , along the permeator length as well as at all radial locations in the fiber bundle.
3. There is no mass transfer resistance in the gas phases.
4. There is negligible diffusion along the mean gas flow path compared to the bulk gas flow.
5. Plug flow model can be used for both gas streams.
6. Pressure drops through fiber lumen are governed by the Hagen-Poiseuille equation.
7. The viscosity of pure gas or gas mixture is independent of pressure but the gas mixture viscosities are dependent on mixture composition.
8. Axial diffusion in the stationary membrane liquid is insignificant compared to the radial diffusion.
9. End effects inside the permeator are negligible.
10. There is negligible deformation of the hollow fibers under external pressure.
11. Separation or pressure drop is unaffected by the small movement of the membrane liquid (due to replenishment of membrane liquid lost by evaporation and/or leakage through defective fibers).

Permeability coefficient of a reactive species, for example, CO_2 , through aqueous solution DEA is strongly dependent on the partial pressure of the gas species at the feed and sweep (or permeate) sides. A detailed analysis is given in a latter part of this section.

ANALYSIS OF GAS MIXTURE SEPARATION IN A HFCLM PERMEATOR

SWEEP GAS MODE OF OPERATION

The mathematical analysis of model biogas mixture separation with a sweep gas in a HFCLM permeator having feed and sweep fibers of different dimensions is considered here. A schematic of the hollow-fiber-contained liquid membrane permeator under sweep gas mode of operation is presented in Figure 2-1. Only one feed fiber and one sweep fiber of different dimensions are shown for simplicity. Different numbers of each kind of fiber were needed to maintain the same permeation area in feed side and sweep side. The sweep gas stream flows countercurrent to the feed gas stream. A binary mixture of CO_2 and N_2 (or CH_4) is used as feed whereas pure helium (or N_2) is used as sweep.

An overall material balance between the feed inlet end and any location at a distance 'l' from the sweep inlet end leads to

$$N_F L - N_S V = N_F L_f - N_S V_f \quad (2-1)$$

Here L and V are local molar feed and sweep flow rates per fiber; N_F and N_S are total number of feed and sweep fibers, respectively. The component balances can be written as

$$\text{CO}_2: \quad N_F Lx - N_S Vy = N_F L_f x_f - N_S V_f y_f \quad (2-2)$$

$$\text{N}_2 \text{ (or CH}_4\text{)}: \quad N_F L(1-x-u) - N_S V(1-y-v) = N_F L_f(1-x_f-u_f) - N_S V_f(1-y_f-v_f) \quad (2-3)$$

$$\text{He (or N}_2\text{)}: \quad N_F Lu - N_S Vv = N_F L_f u_f - N_S V_f v_f \quad (2-4)$$

For equal permeation areas in feed and sweep sides, one can write

$$N_F \pi D_{F0} l_t = N_S \pi D_{S0} l_t \quad (2-5)$$

$$\text{Therefore} \quad N_F/N_S = D_{S0}/D_{F0} = \theta \text{ (say)} \quad (2-6)$$

FIGURE 2-1
 SCHEMATIC OF A HFCLM PERMEATOR FOR MODELING
 SWEEP GAS MODE OF OPERATION

If the axial coordinate 'l' is positive in the direction of sweep gas flow, the governing differential equations for permeation for three species are given by

$$\text{CO}_2: \quad d(Lx)/dl = \pi D_{FO} (Q_a/d) [Px-py] \quad (2-7)$$

$$\text{N}_2 \text{ (or CH}_4\text{): } d[L(1-x-u)]/dl = \pi D_{FO} (Q_b/d) [P(1-x-u)-p(1-y-v)] \quad (2-8)$$

$$\text{He (or N}_2\text{): } d(Lu)/dl = \pi D_{FO} (Q_c/d) [Pu-pv] \quad (2-9)$$

The differential equations governing the pressure drop in the two gas streams in the two sets of fiber lumina are :

$$\text{Feed side : } dP/dl = 128 R T L \mu_F / [\pi P D_{FI}^4] \quad (2-10)$$

$$\text{Sweep side : } dp/dl = - 128 R T V \mu_S / [\pi p D_{SI}^4] \quad (2-11)$$

Eqs. (2-7) through (2-11) may be converted to dimensionless forms as follows:

$$d(L^*x)/dS = \alpha_a [\gamma_1 x - \gamma_2 y] \quad (2-12)$$

$$d[L^*(1-x-u)]/dS = \alpha_b [\gamma_1(1-x-u) - \gamma_2(1-y-v)] \quad (2-13)$$

$$d(L^*u)/dS = \alpha_c [\gamma_1 u - \gamma_2 v] \quad (2-14)$$

$$d\gamma_1/dS = \beta \mu_F^* L^*/\gamma_1 \quad (2-15)$$

$$d\gamma_2/dS = - \beta (D_{FI}/D_{SI})^4 \mu_S^* V^*/\gamma_2 \quad (2-16)$$

where dimensionless area,

$$S = \pi D_{FO} (Q_{ref}/d) (P_{ref}/L_{ref}) l \quad (2-17)$$

dimensionless pressures,

$$\gamma_1 = P/P_{ref} ; \gamma_2 = p/P_{ref} \quad (2-18)$$

dimensionless flow rates,

$$L^* = L/L_{\text{ref}} ; V^* = V/L_{\text{ref}} \quad (2-19)$$

dimensionless viscosities,

$$\mu_F^* = \mu_F/\mu_{\text{ref}} ; \mu_S^* = \mu_S/\mu_{\text{ref}} \quad (2-20)$$

$$\alpha_a = Q_a/Q_{\text{ref}} ; \alpha_b = Q_b/Q_{\text{ref}} ; \alpha_c = Q_c/Q_{\text{ref}} \quad (2-21)$$

and

$$\beta = 128 R T L_{\text{ref}}^2 \mu_{\text{ref}} / [\pi^2 D_{\text{FI}}^4 D_{\text{FO}} (Q_{\text{ref}}/d) P_{\text{ref}}^3] \quad (2-22)$$

Adding Eqs. (2-12), (2-13) and (2-14), one gets

$$dL^*/dS = \alpha_a [\gamma_1 x - \gamma_2 y] + \alpha_b [\gamma_1 (1-x-u) - \gamma_2 (1-y-v)] + \alpha_c [\gamma_1 u - \gamma_2 v] \quad (2-23)$$

From Eqs. (2-1) and (2-2)

$$N_F dL = N_S dV ; N_F d(Lx) = N_S d(Vy)$$

which leads to

$$dV^*/dS = \theta dL^*/dS ; d(V^*_y)/dS = \theta d(L^*_x)/dS$$

Therefore,

$$dV^*/dS = \theta [\alpha_a \{\gamma_1 x - \gamma_2 y\} + \alpha_b \{\gamma_1 (1-x-u) - \gamma_2 (1-y-v)\} + \alpha_c \{\gamma_1 u - \gamma_2 v\}] \quad (2-24)$$

Now, it should be noted that

$$L^* dx/dS = d(L^*_x)/dS - x dL^*/dS$$

$$V^* dy/dS = d(V^*_y)/dS - y dV^*/dS$$

Combining these mathematical relations and Eqs. (2-12), (2-23) and (2-24), one can get

$$dx/dS = [\alpha_a(1-x)(\gamma_1 x - \gamma_2 y) - \alpha_b x \{\gamma_1(1-x-u) - \gamma_2(1-y-v)\} - \alpha_c x(\gamma_1 u - \gamma_2 v)]/L^* \quad (2-25)$$

and

$$dy/dS = \theta[\alpha_a(1-y)(\gamma_1 x - \gamma_2 y) - \alpha_b y \{\gamma_1(1-x-u) - \gamma_2(1-y-v)\} - \alpha_c y(\gamma_1 u - \gamma_2 v)]/V^* \quad (2-26)$$

Following a similar approach, one can also derive,

$$du/dS = [-\alpha_a u(\gamma_1 x - \gamma_2 y) - \alpha_b u \{\gamma_1(1-x-u) - \gamma_2(1-y-v)\} + \alpha_c(1-u)(\gamma_1 u - \gamma_2 v)]/L^* \quad (2-27)$$

$$dv/dS = \theta[-\alpha_a v(\gamma_1 x - \gamma_2 y) - \alpha_b v \{\gamma_1(1-x-u) - \gamma_2(1-y-v)\} + \alpha_c(1-v)(\gamma_1 u - \gamma_2 v)]/V^* \quad (2-28)$$

Equations (2-23) through (2-28), (2-15) and (2-16) constitute a set of eight nonlinear coupled ordinary differential equations in V^* , L^* , y , x , v , u , γ_1 and γ_2 which have to be solved simultaneously using the proper boundary conditions at $l=0$ and $l=l_t$. Generally, it is convenient to specify the domain of the independent variable between 0 and 1. In this case, the total dimensionless area S_t (for $l = l_t$) can be made equal to unity with proper choice of reference parameters (i.e., Q_{ref} , P_{ref} and L_{ref}) in definition (2-17) (Majumdar, 1986). The boundary conditions for the above set of equations can then be written as

$$S = 0 \Rightarrow V^* = V_w^*; y = 0 (= y_w); v = 1 (= v_w) \quad (2-29)$$

$$S = 1 \Rightarrow L^* = L_f^*; x = x_f; u = 0 (= u_f); \gamma_1 = \gamma_{1f}; \gamma_2 = \gamma_{2f} \quad (2-30)$$

The other unknown boundary values such as L_w^* , x_w , u_w , γ_{1w} , γ_{2w} (at $S = 0$) and V_f^* , y_f , v_f (at $S = 1$) were obtained by solving the system of differential equations numerically.

The gas mixture viscosities used in the above and subsequent analyses were computed according to the following equation (Reid et al., 1977) :

$$\bar{\mu} = \sum_i [z_i \mu_i / \sum_j \phi_{ij} z_j] \quad (2-31)$$

where the constants ϕ_{ij} -s are obtained as (Wilke, 1950) :

$$\phi_{ij} = [1 + (\mu_i/\mu_j)^{1/2} (M_{wj}/M_{wi})^{1/4}]^2 / [8(1 + M_{wi}/M_{wj})]^{1/2} \quad (2-32)$$

Here z_i , μ_i , M_{wi} are the mole fraction, viscosity and the molecular weight of the i th species, respectively.

CONVENTIONAL OR VACUUM MODE OF OPERATION

Figure 2-2 shows the schematic of vacuum or conventional mode of membrane gas separation with countercurrent flow. The governing equations for these two modes of operation are identical. Note that these two modes do not utilize any sweep gas; therefore the feed or the permeate gas stream is considered to be a mixture of two components only. The governing differential equations in dimensionless form are easily obtained by putting $u=0$ and $v=0$ [i.e., no helium (or nitrogen in the case of CH_4 in feed) in feed and permeate stream] in Eqs. (2-23) through (2-26), (2-15) and (2-16). The new reduced equations are

$$dL^*/dS = \alpha_a [\gamma_1 x - \gamma_2 y] + \alpha_b [\gamma_1 (1-x) - \gamma_2 (1-y)] \quad (2-33)$$

$$dV^*/dS = \theta [\alpha_a \{\gamma_1 x - \gamma_2 y\} + \alpha_b \{\gamma_1 (1-x) - \gamma_2 (1-y)\}] \quad (2-34)$$

$$dy/dS = \theta [\alpha_a (1-y)(\gamma_1 x - \gamma_2 y) - \alpha_b y \{\gamma_1 (1-x) - \gamma_2 (1-y)\}] / V^* \quad (2-35)$$

$$dx/dS = [\alpha_a (1-x)(\gamma_1 x - \gamma_2 y) - \alpha_b x \{\gamma_1 (1-x) - \gamma_2 (1-y)\}] / L^* \quad (2-36)$$

$$d\gamma_1/dS = \beta \mu_F^* L^* / \gamma_1 \quad (2-37)$$

$$d\gamma_2/dS = -\beta (D_{FI}/D_{SI})^4 \mu_P^* V^* / \gamma_2 \quad (2-38)$$

In Eq. (2-38), subscript 'P' is used to identify the permeate stream. The boundary conditions for the above set of equations are :

$$\text{at } S = 0 \Rightarrow V^* = 0 (= V_w^*); y = y_w = y(\gamma_1, \gamma_2, x) \quad (2-39)$$

and

$$\text{at } S = 1 \Rightarrow L^* = L_f^*; x = x_f; \gamma_1 = \gamma_{1f}; \gamma_2 = \gamma_{2f} \quad (2-40)$$

Since y_w can not be specified explicitly, it has to be determined from other equations.

FIGURE 2-2
SCHEMATIC OF A HFCLM PERMEATOR FOR MODELING
VACUUM OR CONVENTIONAL MODE OF OPERATION

We can write the permeation equations for two components as follows:

$$d(V^*y)/dS = \theta \alpha_a \{\gamma_1x - \gamma_2y\} \quad (2-41)$$

$$d[V^*(1-y)]/dS = \theta \alpha_b \{\gamma_1(1-x) - \gamma_2(1-y)\} \quad (2-42)$$

Dividing Eq. (2-41) by Eq. (2-42) yields

$$\begin{aligned} (V^* dy + y dV^*)/[V^* d(1-y) + (1-y) dV^*] \\ = [\alpha_a \{\gamma_1x - \gamma_2y\}]/[\alpha_b \{\gamma_1(1-x) - \gamma_2(1-y)\}] \end{aligned} \quad (2-43)$$

Applying Eq. (2-43) at $S = 0$ where $V^* = 0$, we get

$$y_w/(1-y_w) = [\alpha_a \{\gamma_{1w}x_w - \gamma_{2w}y_w\}]/[\alpha_b \{\gamma_{1w}(1-x_w) - \gamma_{2w}(1-y_w)\}] \quad (2-44)$$

Thus y_w is determined by solving the above quadratic equation as follows

$$y_w = \frac{\{\alpha_b \gamma_{1w} + (\alpha_a - \alpha_b)(\gamma_{1w}x_w + \gamma_{2w})\} - [\{\alpha_b \gamma_{1w} + (\alpha_a - \alpha_b)(\gamma_{1w}x_w + \gamma_{2w})\}^2 - 4\alpha_a \gamma_{1w} \gamma_{2w} x_w (\alpha_a - \alpha_b)]^{1/2}}{2\gamma_{2w}(\alpha_a - \alpha_b)} \quad (2-45)$$

It should be noted that Eq. (2-35) is indeterminate at $S = 0$. Therefore, L'Hospital rule is applied to determine the derivative at that point by differentiating the numerator and denominator of Eq. (2-35) with respect to 'S'. The equation is given by

$$\begin{aligned} \frac{dy}{dS} \Big|_{S=0} = \frac{\theta \left[\alpha_a (1-y_w) \left\{ \gamma_{1w} \frac{dx}{dS} \Big|_{S=0} + x_w \frac{d\gamma_1}{dS} \Big|_{S=0} - y_w \frac{d\gamma_2}{dS} \Big|_{S=0} \right\} - \right. \\ \left. \alpha_b y_w \left\{ -\gamma_{1w} \frac{dx}{dS} \Big|_{S=0} + (1-x_w) \frac{d\gamma_1}{dS} \Big|_{S=0} - (1-y_w) \frac{d\gamma_2}{dS} \Big|_{S=0} \right\} \right]}{\frac{dV^*}{dS} \Big|_{S=0} + \theta \left[\alpha_a (1-y_w) \gamma_{2w} + \alpha_a \{\gamma_{1w}x_w - \gamma_{2w}y_w\} + \right. \\ \left. \alpha_b \{\gamma_{1w}(1-x_w) - \gamma_{2w}(1-y_w)\} + \alpha_b y_w \gamma_{2w} \right]} \end{aligned} \quad (2-46)$$

Since $V^* = 0$ at $S = 0$, therefore, $\left. \frac{dy}{dS} \right|_{S=0} = 0$ and substituting $\left. \frac{dV^*}{dS} \right|_{S=0}$ from Eq. (2-34) at $S = 0$ in Eq. (2-46) one can get

$$\left. \frac{dy}{dS} \right|_{S=0} = \frac{\left[\left. \frac{dx}{dS} \right|_{S=0} \{ \alpha_a(1-y_w)\gamma_{1w} + \alpha_b y_w \gamma_{1w} \} + \left. \frac{dy_1}{dS} \right|_{S=0} \{ \alpha_a(1-y_w)x_w - \alpha_b(1-x_w)y_w \} \right]}{\left[\begin{array}{l} 2(\alpha_a - \alpha_b)\gamma_{1w}x_w + \alpha_a\gamma_{2w} \\ -3(\alpha_a - \alpha_b)\gamma_{2w}y_w + 2\{\alpha_b(\gamma_{1w} - \gamma_{2w})\} \end{array} \right]} \quad (2-47)$$

SWEEP WATER MODE OF OPERATION

The schematic for this particular configuration is shown in Figure 2-3. Here, fresh water is introduced countercurrent to the feed gas mixture through the bore of sweep fibers. In this mode, permeating gases first desorb from the stationary liquid membrane at the permeate side, then diffuse through the gas phase confined in the pores of the microporous wall of the hollow fiber and are finally absorbed in the flowing sweep water. For modeling a HFCLM permeator under sweep water mode of operation, the following additional assumptions, apart from those considered earlier, are necessary:

1. There is no gas phase mass transfer resistance in the pores of microporous fiber wall on the sweep water side.
2. The gas pressure p_i and gas composition y_i inside the pores of the microporous fiber wall of sweep water side controls the permeation process; the sweep water pressure has no effect.

The governing differential equations for permeation for the two species are given by

$$CO_2: \quad d(Lx)/dl = \pi D_{FO} (Q_a/d) [Px - p_i y_i] \quad (2-48)$$

$$N_2 \text{ (or } CH_4\text{): } d[L(1-x)]/dl = \pi D_{FO} (Q_b/d) [P(1-x) - p_i(1-y_i)] \quad (2-49)$$

FIGURE 2-3
 SCHEMATIC OF A HFCLM PERMEATOR FOR MODELING
 SWEEP WATER MODE OF OPERATION

The water side governing equations for the two species with q , the water flow rate/fiber, can be written as

$$\text{CO}_2: \quad q \, dC_a/dl = (k_m)_a [S_a p_i y_i - C_a] \pi D_{SI} \quad (2-50)$$

$$\text{N}_2 \text{ (or CH}_4\text{)}: \quad q \, dC_b/dl = (k_m)_b [S_b p_i (1-y_i) - C_b] \pi D_{SI} \quad (2-51)$$

where k_m is obtained either from the local value of Sherwood number based on local concentration difference, or the Sherwood number based on the arithmetic-mean concentration difference (Skelland, 1974)

$$(N_{Sh_i})_l = \{(k_m)_i \mid_1 D_{SI} / D_i\} = f_{1i} \quad (2-52)$$

$$\text{where } f_{1i} = \frac{\{ \sum_{j=1}^{\infty} (B_j/2) (d\phi_j/dr_+)_{r_+=1} \exp\{-\beta_j^2 (2l_t/D_{SI})/N_{Re} N_{Sc_i}\} \}}{2 \{ \sum_{j=1}^{\infty} (B_j/2\beta_j^2) (d\phi_j/dr_+)_{r_+=1} \exp\{-\beta_j^2 (2l_t/D_{SI})/N_{Re} N_{Sc_i}\} \}} \quad (2-53)$$

$$\text{and } (N_{Sh_i})_{avg} = \{(k_m)_i \mid_{avg} D_{SI} / D_i\} = 0.5 (D_{SI}/l_t) N_{Re} N_{Sc_i} f_{2i} \quad (2-54)$$

$$\text{where } f_{2i} = \frac{1 - \{ \sum_{j=1}^{\infty} (-4B_j/\beta_j^2) (d\phi_j/dr_+)_{r_+=1} \exp\{-\beta_j^2 (2l_t/D_{SI})/N_{Re} N_{Sc_i}\} \}}{1 + \{ \sum_{j=1}^{\infty} (-4B_j/\beta_j^2) (d\phi_j/dr_+)_{r_+=1} \exp\{-\beta_j^2 (2l_t/D_{SI})/N_{Re} N_{Sc_i}\} \}} \quad (2-55)$$

$$\text{where } \beta_j = 4(j-1) + (8/3) \quad ; \quad j = 1, 2, 3, \dots \quad (2-56)$$

$$\text{and } (-B_j/2) (d\phi_j/dr_+)_{r_+=1} = 1.01276 \beta_j^{-1/3} \quad (2-57)$$

The differential equations governing the pressure drops through the two different fiber sets are:

$$\text{Feed side : } dP/dl = 128 R T L \mu_F / [\pi P D_{FI}^4] \quad (2-58)$$

$$\text{Sweep side : } dp_w/dl = - 128 q \mu_w / [\pi D_{SI}^4] \quad (2-59)$$

Equations (2-48) to (2-51), (2-58) and (2-59) are converted to dimensionless forms as follows :

$$d(L^*x)/dS = \alpha [\gamma_1 x - \gamma_i y_i] \quad (2-60)$$

$$d[L^*(1-x)]/dS = [\gamma_1(1-x) - \gamma_i(1-y_i)] \quad (2-61)$$

$$dC_a^*/dS = R_a [s \gamma_i y_i - C_a^*] \quad (2-62)$$

$$dC_b^*/dS = R_b [\gamma_i(1-y_i) - C_b^*] \quad (2-63)$$

$$d\gamma_1/dS = \beta_F \mu_F^* L^*/\gamma_1 \quad (2-64)$$

$$d\gamma_w/dS = -\beta_S \quad (2-65)$$

where

$$\gamma_1 = P_f/P_{ref}; \gamma_w = P_w/P_{ref}; \gamma_i = P_i/P_{ref} \quad (2-66)$$

$$C_a^* = C_a/(S_b P_{ref}); C_b^* = C_b/(S_b P_{ref}) \quad (2-67)$$

$$\alpha = Q_a/Q_b; s = S_a/S_b \quad (2-68)$$

$$\beta_F = 128 R T L_{ref}^2 \mu_{ref}/\{\pi^2 D_{FI}^4 D_{FO} (Q_b/d) P_{ref}^3\} \quad (2-69)$$

$$\beta_S = 128 \mu_w q L_{ref}/\{\pi^2 D_{SI}^4 D_{FO} (Q_b/d) P_{ref}^2\} \quad (2-70)$$

$$R_a = \{(k_m)_a D_{SI} L_{ref}\}/\{(Q_b/d) D_{FO} q P_{ref}\} \quad (2-71)$$

and

$$R_b = \{(k_m)_b D_{SI} L_{ref}\}/\{(Q_b/d) D_{FO} q P_{ref}\} \quad (2-72)$$

From Eqs. (2-60) and (2-61) one can easily get

$$dL^*/dS = \alpha [\gamma_1 x - \gamma_i y_i] + [\gamma_1(1-x) - \gamma_i(1-y_i)] \quad (2-73)$$

and

$$dx/dS = [\alpha(1-x)(\gamma_1 x - \gamma_i y_i) - x\{\gamma_1(1-x) - \gamma_i(1-y_i)\}]/L^* \quad (2-74)$$

From CO₂ balance, we can write

$$N_F d(Lx)/dl = N_S q dC_a/dl \quad (2-75)$$

Similarly, from N_2 (or CH_4) balance

$$N_F d[L(1-x)]/dl = N_S q dC_b/dl \quad (2-76)$$

Equations (2-75) and (2-76) along with Eqs. (2-60) to (2-63) lead to

$$\gamma_1 x - \gamma_i y_i = \psi_1 [s \gamma_i y_i - C_a^*] \quad (2-77)$$

$$\gamma_1 (1-x) - \gamma_i (1-y_i) = \psi_2 [\gamma_i (1-y_i) - C_b^*] \quad (2-78)$$

$$\text{where } \psi_1 = \{D_{SI} N_S (k_m)_a S_b\} / \{D_{FO} N_F (Q_a/d)\} \quad (2-79)$$

$$\text{and } \psi_2 = \{D_{SI} N_S (k_m)_b S_b\} / \{D_{FO} N_F (Q_b/d)\} \quad (2-80)$$

Solving Eqs. (2-77) and (2-78) for y_i and γ_i in terms of x and γ_1 , one gets locally

$$y_i = (\psi_1 C_a^* + \gamma_1 x) / \{\gamma_i (1 + \psi_1 s)\} \quad (2-81)$$

$$\text{and } \gamma_i = \frac{[1 + \psi_1 s] [\gamma_1 (1-x) + \psi_2 C_b^*] + (\psi_2 + 1)(\psi_1 C_a^* + \gamma_1 x)}{(1 + \psi_1 s) (\psi_2 + 1)} \quad (2-82)$$

Using above two equations for y_i and γ_i , the nonlinear coupled differential Eqs. (2-62), (2-63), (2-64), (2-65), (2-73) and (2-74) have to be solved simultaneously with the following boundary conditions:

$$S = 0 \Rightarrow C_a^* = C_{aw}^*; C_b^* = C_{bw}^* \quad (2-83)$$

$$S = 1 \Rightarrow L^* = L_f^*, x = x_f; \gamma_1 = \gamma_{1f}; \gamma_w = \gamma_{wf} \quad (2-84)$$

The quantities C_{aw}^* and C_{bw}^* are the dimensionless dissolved CO_2 and N_2 (or CH_4) concentrations in fresh water, respectively. The value of C_{bw}^* is equal to zero

for the particular case of CH_4 .

DETERMINATION OF EFFECTIVE MEMBRANE THICKNESS IN A HFCLM PERMEATOR

Effective membrane thickness for each permeator is determined from pure component permeation runs under conventional mode of operation with pure CO_2 as feed gas and water as membrane liquid. For pure CO_2 permeation, the governing differential equations for conventional mode of operation, where the permeate is withdrawn countercurrent to the feed stream, reduce to

$$dL^*/dS = \alpha_a [\gamma_1 - \gamma_2] \quad (2-85)$$

$$dV^*/dS = \theta \alpha_a [\gamma_1 - \gamma_2] \quad (2-86)$$

$$d\gamma_1/dS = \beta \mu_F^* L^*/\gamma_1 \quad (2-87)$$

$$d\gamma_2/dS = -\beta (D_{FI}/D_{SI})^4 \mu_P^* V^*/\gamma_2 \quad (2-88)$$

The boundary conditions for the above set of equations are :

$$\text{at } S = 0 \Rightarrow V^* = 0 (= V_w^*) \quad (2-89)$$

and

$$\text{at } S = 1 \Rightarrow L^* = L_f^*; \gamma_1 = \gamma_{1f}; \gamma_2 = \gamma_{2f} \quad (2-90)$$

Since the permeability value of CO_2 through water is known, Eqs. (2-85) to (2-88) are solved simultaneously for different values of effective membrane thickness (d). The correct value of d should match the numerical results with experimental permeation rate.

DETERMINATION OF PERMEABILITY OF A NONREACTIVE SPECIES THROUGH AN AQUEOUS SOLUTION OF DEA

The permeability of CO_2 through an aqueous solution of DEA may be determined from the facilitated transport analysis, described later. However, the permeability of a nonreactive gas species (e.g., N_2 or He) through an aqueous solution of DEA is determined from pure component permeation runs under

conventional mode of operation. The governing differential equations for the i-th species in dimensionless form under conventional mode of operation, where the permeate stream is withdrawn cocurrent to the feed stream, can be written as follows (with the coordinate being measured from feed entrance along the permeator):

$$dL^*/dS = - \alpha_i [\gamma_1 - \gamma_2] \quad (2-91)$$

$$dV^*/dS = \theta \alpha_i [\gamma_1 - \gamma_2] \quad (2-92)$$

$$d\gamma_1/dS = - \beta \mu_F^* L^*/\gamma_1 \quad (2-93)$$

$$d\gamma_2/dS = - \beta (D_{FI}/D_{SI})^4 \mu_P^* V^*/\gamma_2 \quad (2-94)$$

The boundary conditions for the above set of equations are :

$$\text{at } S = 0 \Rightarrow L^* = L_f^*; \gamma_1 = \gamma_{1f}; V^* = 0 (= V_w^*) \quad (2-95)$$

and

$$\text{at } S = 1 \Rightarrow \gamma_2 = \gamma_{2w} \quad (2-96)$$

Since the effective membrane thickness of the permeator is known, the above Eqs. (2-91) to (2-94) are solved simultaneously for different values of species permeability. The correct value of permeability should match the numerical results with the experimental permeation rate.

ANALYSIS OF FACILITATED TRANSPORT OF CO₂ THROUGH AN AQUEOUS SOLUTION OF DEA

In the aqueous solution of DEA the following reactions occur with CO₂:

with the overall reaction being

Here DEA is represented as R_2NH . Since reaction (2-98) is considerably faster compared to reaction (2-97) (Danckwerts and Sharma, 1966), it is assumed to be at equilibrium. Thus reaction (2-97) controls the transport (Donaldson and Nguyen, 1980), and the rate of reaction can be written as (Blanc and Demarais, 1984)

$$r_{\text{CO}_2} = k_{\text{Am}} [\text{R}_2\text{NH}] [\text{CO}_2] - \frac{k_{\text{Am}}}{K_{\text{Am}}} [\text{R}_2\text{NCOO}^-] [\text{H}^+] \quad (2-100)$$

where the bracket designates the molar concentration and

$$K_{\text{Am}} = \frac{[\text{R}_2\text{NCOO}^-] [\text{H}^+]}{[\text{R}_2\text{NH}] [\text{CO}_2]} \quad (2-101)$$

Further the equilibrium constant of the reaction (2-98) can be written as

$$K_p = \frac{[\text{R}_2\text{NH}_2^+]}{[\text{R}_2\text{NH}] [\text{H}^+]} \quad (2-102)$$

At steady state, local CO_2 balance leads to

$$D_{1\text{Am}} \frac{d^2[\text{CO}_2]}{dz^2} = r_{\text{CO}_2} \quad (2-103)$$

Neglecting $[\text{H}^+]$ contribution, electroneutrality condition at any point can be written as

$$[\text{R}_2\text{NCOO}^-] = [\text{R}_2\text{NH}_2^+] \quad (2-104)$$

Thus for free amine

$$D_{R_2NH} \frac{d^2 [R_2NH]}{dz^2} = 2 r_{CO_2} \quad (2-105)$$

Assuming equal diffusivity of all the species other than CO_2 leads to

$$[R_2NH] + [R_2NCOO^-] + [R_2NH_2^+] = C_T \quad (2-106)$$

where C_T is the initial amine concentration.

Combining Eqs. (2-104) and (2-106) one can get

$$[R_2NH_2^+] = (C_T - [R_2NH])/2 \quad (2-107)$$

Combining Eqs. (2-100), (2-102) and (2-107) and expressing the reaction rate in terms of dissolved carbon dioxide and free amine we get

$$r_{CO_2} = k_{Am} [R_2NH] [CO_2] - \frac{k_{Am} \{ C_T - [R_2NH] \}^2}{4 K_{Am} K_P [R_2NH]} \quad (2-108)$$

Equation (2-103) can now be expressed as

$$D_{1Am} \frac{d^2 [CO_2]}{dz^2} = k_{Am} [R_2NH] [CO_2] - \frac{k_{Am} \{ C_T - [R_2NH] \}^2}{4 K_{Am} K_P [R_2NH]} \quad (2-109)$$

Similarly for free amine

$$\begin{aligned} D_{R_2NH} \frac{d^2 [R_2NH]}{dz^2} &= 2 r_{CO_2} \\ &= 2 k_{Am} [R_2NH] [CO_2] - \frac{k_{Am} \{ C_T - [R_2NH] \}^2}{2 K_{Am} K_P [R_2NH]} \end{aligned} \quad (2-110)$$

Equations (2-109) and (2-110) are to be solved along with the following boundary conditions

$$\text{at } z=0 \quad [\text{CO}_2] = H_{1\text{Am}} P_u ; d[\text{R}_2\text{NH}]/dz = 0$$

$$\text{at } z=d \quad [\text{CO}_2] = H_{1\text{Am}} P_d ; d[\text{R}_2\text{NH}]/dz = 0$$

where $H_{1\text{Am}}$ is the Henry's law constant for CO_2 in aqueous DEA solution; P_u and P_d are the upstream and downstream partial pressures of CO_2 across the liquid membrane, respectively.

Equations (2-109) and (2-110) as well as the boundary conditions can be made dimensionless as follows

$$\frac{d^2 C_3}{d\xi^2} = q_1 C_3 C_4 - q_2 \frac{(1-C_4)^2}{C_4} \quad (2-111)$$

$$\frac{d^2 C_4}{d\xi^2} = q_3 C_3 C_4 - q_4 \frac{(1-C_4)^2}{C_4} \quad (2-112)$$

where

$$C_3 = [\text{CO}_2] / (H_{1\text{Am}} P_u) ; C_4 = [\text{R}_2\text{NH}] / C_T ; \xi = (z/d) \quad (2-113)$$

$$q_1 = k_{\text{Am}} C_T d^2 / D_{1\text{Am}} \quad (2-114)$$

$$q_2 = k_{\text{Am}} C_T d^2 / (4 K_{\text{Am}} K_P D_{1\text{Am}} H_{1\text{Am}} P_u) \quad (2-115)$$

$$q_3 = 2 k_{\text{Am}} H_{1\text{Am}} P_u d^2 / D_{\text{R}_2\text{NH}} \quad (2-116)$$

$$q_4 = k_{\text{Am}} d^2 / (2 K_{\text{Am}} K_P D_{\text{R}_2\text{NH}}) \quad (2-117)$$

Equations (2-111) and (2-112) are to be solved along with the following boundary conditions

$$\xi = 0 \Rightarrow C_3 = 1 ; \quad dC_4/d\xi = 0 \quad (2-118)$$

$$\xi = 1 \Rightarrow C_3 = P_d/P_u ; \quad dC_4/d\xi = 0 \quad (2-119)$$

Once the solution for C_3 and C_4 are known, the facilitation factor F_{Am} and the effective permeability of CO_2 corresponding to the partial pressures of CO_2 (P_u and P_d) can be calculated as follows:

$$\text{Total Flux} = N_{CO_2} + \frac{1}{2} N_{R_2NH} \quad (2-120)$$

$$F_{Am} = \frac{1}{2} \frac{D_{R_2NH} C_T \{ C_4(1) - C_4(0) \}}{D_{1Am} H_{1Am} (P_u - P_d)} \quad (2-121)$$

$$Q_{1Am} = D_{1Am} H_{1Am} (1 + F_{Am}) \quad (2-122)$$

SIMULATION TECHNIQUES FOR SEPARATION PROBLEMS IN HFCLM PERMEATOR

The gas separation problems in HFCLM permeator under all four modes involved ordinary nonlinear coupled differential equations. These are all boundary value (BV) problems as the feed and sweep (or permeate) gas or sweep liquid stream flows in a countercurrent fashion in all cases. Thus the solution procedures are the same for all modes of operation. Determination of effective membrane thickness as well as pure component permeability from pure component permeation runs also involve the solution of boundary value problems.

IMSL subroutine DVCPR was used to solve the BV problems. The subroutine DVCPR is based on PASVA3 program (Pereyra, 1978), a finite difference method. However, to use the routine successfully one had to supply an initial estimate for each of the dependent variables at the selected grid points along the domain of the independent variable. The method of generating the initial guess was the same in all the problems. The system of differential equations was solved as an initial value problem by imposing the conditions of cocurrent flow pattern and negligible pressure drop in the sweep (or permeate) side. IMSL routine DVERK was used to solve the initial value problem. The routine uses

Runge Kutta formula of order 5 and 6 developed by Verner (Jackson et al., 1976). Once the initial value problem was solved then the estimates were used for subsequent solution of the actual BV problem by DVCPR routine (Sengupta, 1985; Majumdar, 1986).

SOLUTION PROCEDURE FOR FACILITATED TRANSPORT ANALYSIS

The analysis of facilitated transport of CO_2 through an aqueous solution of DEA results in two second order ordinary differential equations. These are highly nonlinear boundary value problems and have enjoyed considerable attention since no exact solutions exist. Two approaches have been used for the solution; semianalytical and numerical. The semianalytical methods are based on matched asymptotic expansions (Goddard et al., 1970; Kruezer and Hoofd, 1970; Smith et al., 1973), regular perturbation method (Suchdeo and Schultz, 1974), and techniques involving other approximations to the differential equations (Friedlander and Keller, 1965; Otto and Quinn, 1971; Donaldson and Quinn, 1975; Smith and Quinn, 1979; Hoofd and Kruezer, 1981). The numerical methods involve the quasilinearization technique (Kutchai et al., 1970; Suchdeo and Schultz, 1974), a finite difference technique with nonuniform mesh size (Nedelman and Rubinow, 1981) and a technique based on the Galerkin method (Ward, 1970). More recently Jain and Schultz (1982) solved the problem numerically by a technique based on orthogonal collocation on finite elements introduced by Carey and Finlayson (1975). However, the solution procedure is more complex. A simpler numerical solution procedure was adopted here.

Complete numerical solution of the facilitated transport equations involved the following steps. At first, the two second order differential equations were converted into four first order ordinary differential equations. Then the system of equations were solved by using IMSL routine DVCPR. In this particular case initial guess was generated by assuming that all the reactions were at equilibrium. Once the initial guesses were generated for all the variables, the problem was solved by DVCPR routine (Guha, 1989).

GENERALIZED TWO DIMENSIONAL MODEL FOR MEMBRANE THICKNESS DETERMINATION

A generalized computer program has been developed to estimate the effective

membrane thickness (EMT) for the HFCLM (hollow-fiber-contained liquid membrane) module in which no chemical reactions were occurring. The computer program based on a 2-dimensional diffusion analysis presented in the NYSERDA Report 87-10 could not be used directly for calculation of an EMT for different outer diameters (O.D.) of fibers without modification. It is useful to generalize the computer program so that EMT can be calculated immediately whenever the outside diameter of the fiber is given. This will allow module design and analysis for other fiber sizes that may be obtained in future.

To achieve this goal, it is necessary to develop several techniques in addition to the algorithm presented in NYSERDA Report No. 87-10. First, the boundary points are created automatically along the given circle and the identification numbers are assigned to each boundary grid point depending on the type as shown in Figure 2-4. Boundary grid points can be grouped into four categories. Variables "a" and "b" refer to the horizontal fractional intercept and the vertical fractional intercept, respectively of the unit grid dimension. EPS indicates the tolerance of "a" and "b." When the magnitudes of "a" and "b" are both less than the value of EPS, the grid point is located on the curved boundary. Values of "a" and "b" are computed at each boundary grid point and are incorporated in calculating the dimensionless concentration. Since one square pitch cell is constructed of four quarter circles of radii R_1 , R_2 , R_3 and R_4 , as shown in Figure 2-5, four subroutines were developed.

Second, once all the boundary points are identified, the interior points are identified with ID number zero. The next step is to solve the governing partial differential equation. For computer calculations, a finite difference method is used with Liebmann's iterative scheme (Chow, 1979). Such iteration formula at the interior grid point (i,j) can be written as

$$C_{i,j}^{n+1} = (1/4) * [C_{i-1,j}^{n+1} + C_{i+1,j}^n + C_{i,j-1}^{n+1} + C_{i,j+1}^n] \quad (2-123)$$

where the superscripts denote the number of iterations. At the boundary points as shown in Figure 2-4, the corresponding iteration formula is

$$C_{i,j}^{n+1} = [C_A / \{a(a+1)\} + C_B / \{b(b+1)\} + C_{i-1,j}^{n+1} / (a+1) + C_{i,j+1}^n / (b+1)] * [ab / (a+b)] \quad (2-124)$$

Circle

Type 1

ID = 1

$\text{eps} < a < 1$
 $\text{eps} < b < 1$

Type 2

ID = 2

$a = 1$
 $\text{eps} < b < 1$

Type 3

ID = 3

$\text{eps} < a < 1$
 $b = 1$

Type 4

ID = 4

$0 \leq a \leq \text{eps}$
 $0 \leq b \leq \text{eps}$

R_1

R_2

R_3

R_4

Type 0

ID = 0

Interior Grid
 Points

FIGURE 2-4
 TYPES OF BOUNDARY POINTS

where C_A and C_B refer to the dimensionless concentrations of the neighboring points shown in Figure 2-4. To start the iteration, a constant value of zero is first guessed for the dimensionless concentration at all interior points. With the proper boundary conditions for C shown in Figure 2-6, a new value of C is computed from the above equation at each grid point. The absolute value of the difference between this and the previous value of C at the same grid point is calculated and is added to the value of a variable called ERROR, whose starting value at the beginning of an iteration is zero. At the end of one iteration, this value is compared with maximum allowable value of the total error.

Third, the number of grid points can be adjusted so that the possible error could be reduced to the minimum. When the number of grid points are increased, not only can the boundary grid points be located near the curved boundary, but the accuracy of calculation for the interior points can also be increased. In such a fashion, the dimensionless concentration can be obtained at all grid points.

Finally, the total rate of solute transport per cell per unit length of the permeator can be obtained by a subroutine called 'FLUX.' The effective membrane thickness can be calculated in the same subroutine. The complete listing of the program is given in the Appendix.

The computer program is first applied for the EMT estimation of a permeator module which is made of only one kind of fibers while the fiber size varied. It can be utilized also for estimation of the EMT for a permeator made of mixed fibers; for example, when two different sizes of fibers are used where fibers of one size act as sweep fibers and fibers of other size act as feed fibers.

A schematic diagram of a unit cell consisting of two different sizes of fibers is shown in Figure 2-7. From the geometrical configuration of the permeators #6 and #7 (feed fibers: number = 300, OD = 150 μ m and sweep fibers: number = 155, OD = 290 μ m), the pitch of the square configuration cell (assuming the rhombus to be replaced by a square) is given by

$$\tau = [(D_b - D_{F0}) / (6 N_S)] \{-\pi / (2\sqrt{2}) + \sqrt{\{\pi^2 / 8 + 3 \pi N_S\}}\} \quad (2-125)$$

COMPUTER PROGRAM

BOUNDARY CONDITIONS

LEE1.FOR

LEE2.FOR

LEE3.FOR

LEE4.FOR

FIGURE 2-6
TYPES OF BOUNDARY CONDITIONS

FIGURE 2-7
 SCHEMATIC REPRESENTATION OF A RHOMBOIDAL UNIT CELL
 IN THE MHF BUNDLE ASSEMBLY OF A MIXED FIBER CLM PERMEATOR

Unlike permeators made from fibers of uniform size, there exists greater restrictions in the calculation of the EMT in the mixed fiber permeator. Since the bigger O.D. fibers act as sweep fibers and the smaller O.D. fibers act as feed fibers, there is only one possible symmetrical geometrical arrangement of mixed fibers. Namely, one square cell contains three of one quarter of feed fiber and one quarter of sweep fiber.

For the case of a permeator constructed of the fibers of uniform size, the EMT based on the feed fiber is the same as that based on the sweep fiber. However, the EMT calculated based on the feed fiber is slightly different from that estimated based on the sweep fiber for the permeator made of two kinds of fibers, because the total mass transport rate in a cell remains constant while the available surface area of sweep fiber is different from that of feed fiber in a unit cell.

Section 3

EXPERIMENTAL

In the present investigation, microporous hydrophobic polypropylene Celgard X-10 hollow fibers of 100 micron ID and 240 micron ID were used for fabricating the hollow-fiber-contained liquid membrane permeators. Both of these fibers have bubble point pressures of 150 psi with mean pore sizes of 0.03 micron and thickness of 25 micron. Thus both sizes are suitable for biogas applications, as the separation studies were conducted at an absolute pressure of 60 psi or less depending on the operating mode.

The ideal characteristics for a liquid for the purpose of a membrane in the HFCLM technique are: stable, nonfoaming, relatively low volatility, not highly corrosive and viscous; further, it must have a high solubility for one of the solutes compared with that for the other. In earlier studies of biogas purification, pure water and aqueous solution of K_2CO_3 were used as liquid membranes whereas in the present study more emphasis was given to aqueous solution of organic liquids.

DETERMINATION OF WETTABILITY, BUBBLE POINTS AND BREAKTHROUGH POINTS

It was essential to develop information about certain physical properties of the liquid membrane - microporous substrate system before aqueous solution of organic liquids could be used as membranes in a HFCLM permeator. These are: wettability of the microporous membrane by the membrane liquid, breakthrough pressure and/or bubble point pressure as the case may be. The following organic liquids, monoethanolamine (MEA), diethanolamine (DEA), and 1-methyl-2-pyrrolidinone (NMP) and their aqueous solutions were subjected to such testing.

When the solvent or its solution wetted the microporous polypropylene membrane, the bubble point measurement had to be carried out. On the other hand, if the membrane was not wetted by a given solvent or solution, the solvent breakthrough measurement had to be performed. The bubble point is defined as the pressure of air or nitrogen gas required to force the solvent from the largest wetted pore of a membrane. Generally, the larger the pore, the

lesser is the pressure required to expel the liquid. The solvent breakthrough pressure is the pressure required to transmit the solvent through the largest pore of a membrane not wetted by the solvent.

Such information was generated using Celgard 2400 flat films (Celanese Specialty Operations, Summit, N.J.), the surface characteristics of which are identical to the Celgard hollow fibers. Although the pore sizes of Celgard 2400 are somewhat smaller (0.02 micron) than those of the hollow fibers, it was felt that the information would be sufficient for decision making purposes. As displayed in Table 3-1, the measured breakthrough points were higher than 60 psi in Celgard 2400 for certain solutions. This means that it is safe for the pressure of liquid membrane (i.e., 20 vol% water in NMP or 20 wt% DEA solution in water) to be slightly higher than the highest operating pressure of gas streams (60 psia) in the permeator. There would not be any membrane liquid breakthrough into the sweep fibers under the operating conditions.

FABRICATION OF SMALL-SCALE HFCLM PERMEATORS

The fabrication procedures for first four permeators (#1 to #4) were described in detail in the NYSERDA Report 87-10. Five more small-scale permeators were fabricated during this investigation and were numbered sequentially (e.g., #5 to #9). The detailed geometrical characteristics of each permeator used in this study are given in Table 3-2. The hollow-fiber surface area in the feed side was equal to that of the permeate side in all the permeators.

Fabrication of a permeator involved preparation of fiber bundles and putting them in a shell and finally potting the ends with a resin mixture to form a tube sheet.

For permeator #5, a 9-ft-long mat of 300 fibers (X-10, 150 micron OD) was first prepared on a polyethylene sheet over a laboratory bench top as follows. The bobbin containing the fibers was first exposed to the exhaust from a humidifier to eliminate the static charge on the surface of the fibers. Then six fibers were taken out at a time from the bobbin; they were cut to the desired length using scissors and both ends of the fibers were attached to a strip of scotch tape. Thus 300 fibers, 9 ft long, were placed close to one another to complete

TABLE 3-1

DETERMINATION OF WETTABILITY OF SOLUTIONS IN
CELGARD 2400 POLYPROPYLENE MEMBRANES, BUBBLE POINTS AND
BREAKTHROUGH POINTS THROUGH THE SAME MEMBRANE

Solutions	Wettability	ΔP (psi) Bubble Point	ΔP (psi) Breakthrough Point*
NMP	TW	22.0	-
Water/NMP Mixtures			
5 Vol. % Water	TW	-	-
10 Vol. % Water	PW	-	-
15 Vol. % Water	NW	-	-
20 Vol. % Water	NW	-	60.0
MEA	NW	-	-
DEA	NW	-	-
DEA/Water Mixtures			
20 Wt. % DEA	NW	-	>80.0**
Water***	NW	-	150.0

TW - Totally Wet

PW - Partially Wet

NW - Non Wet

* 100% humidified N_2 gas was introduced at 5 psi in the lower pressure side of the testing cell.

** Maximum possible operating pressure of the testing cell since the pressure vessel has a 110 psi limit.

*** Cited from Celgard catalog

Table 3-2
DETAILED GEOMETRICAL CHARACTERISTICS OF
SMALL-SCALE HFCLM PERMEATORS

Permeator #	Active Length inch	Feed Fiber Total No.	Fiber ID/OD micron	Permeate Fiber Total No.	Fiber ID/OD micron	Void Space %
3	62	300	100/150	300	100/150	66.5
4	62	300	100/150	300	100/150	63.7
5	62	300	100/150	300	100/150	63.7
6	24	300	100/150	155	240/290	46.7
7	24	300	100/150	155	240/290	46.7
8	17	300	100/150	300	100/150	63.7
9	17.5	300	100/150	300	100/150	63.7

one mat. Once such a mat was ready, the mat ends were covered by two polyethylene sheets about 10 inches long. The polyethylene sheets were kept in place by scotch tape outside the region of the mat. Two new pieces of scotch tape were placed on the polyethylene sheets to put another 300 fibers having the same dimensions. These fibers were placed in between the fibers of the previous mat to ensure close proximity between the two sets of fibers. Thus, two sets of fibers were well mixed in the middle section but separated completely at the end by the upper polyethylene sheets.

For permeator #6, one set of fibers consisted of 300, X-10 Celgard hollow fibers of 150 micron outside diameter and the other set consisted of 155, X-10 fibers of 290 micron outside diameter. The total number of fibers in each set was chosen in such a way that the total area of permeation remained equal on both sides (feed and permeate). Preparation of the mat was done exactly in the similar fashion but the total length of each fiber taken was 4 ft with an effective permeator length of 2 feet.

The fiber dimensions for permeator #7 were similar to those of permeator #6. However, the fibers utilized in this permeator were tested for leakage before preparation of the integrated fiber mat. A large number (about 400) of fibers (X-10, 150 micron O.D.), each about 5 ft long, were first potted at each end in a 2-inch-long hexagonal nipple (Cajon) using an epoxy resin mixture prepared with 80:20 ratio of C-4 resin to activator D (Beacon Chemical Co., Mt. Vernon, NY). The hollow fibers were then pressurized internally with water up to a pressure of 50 psig. This type of test was done also for the other set of fibers (X-10, 290 micron O.D.). About 300 fibers were taken for this purpose. A few fibers were found to be defective in each case and were leaking during the test. The leaky fibers were separated and discarded. The fiber mat for the permeator #7 was then prepared with the remaining good fibers in a manner similar to that for permeator #6.

In the case of permeators #8 and #9, the fibers were also pressure tested in a manner similar to that for permeator #7. However, in both cases, fibers of 100 micron ID were used in feed as well as sweep sides. To minimize the handling of fibers one more strip of scotch tape was placed at 6 inches from both the ends, so that when the ends were potted in the nipple for pressure testing they were

still in the form of a mat. Figure 3-1 shows two separate mats with both ends potted in the nipple. After pressure testing, leaky fibers as well as some good fibers were removed to bring the total number of fibers in each mat to exactly 300. Then the mats were cut from the nipples and one mat was placed on the top of the other to make an integrated mat with the ends being separated. The integrated mat was then rolled to prepare the fiber bundle as before. The technique for making the fiber bundle was the same for all the permeators.

Distilled water was sprayed over the mat for easy handling of the fibers. Fibers were slowly gathered together starting from the middle section and gradually approaching the end. Cotton threads (wetted) were tied loosely in the middle section as well as at the four separated ends to keep the fibers together as shown in Figure 3-2. Cotton threads were removed slowly as the fiber bundle was inserted into specially constructed permeator shell. A 1/8-inch teflon pipe (I.D. 0.240 inch, O.D. 0.406 inch; Cole Parmer, Chicago, IL) was inserted into the 1/2-inch schedule 40 stainless steel pipe to make the shell. Epoxy resin was used to fill the annular space between the two concentric pipes. The pipe assembly thus constructed acted as a shell for all the new permeators. The pipe was fitted with a 1/2-inch stainless steel street tee (Cajon) followed by 1/2-inch stainless steel 45° Y-fitting (NJ Engineering & Supply Co., Passaic, NJ) at each end. The end fitting of permeator #5 is shown in Figure 3-3.

The side opening of the street tee was used as a shell side liquid port (entry or exit). The two openings of the Y-fittings were needed to separate the two sets of fibers. Y-fittings have distinct advantage over cross connection (used for permeators #1 to #4; Majumdar, 1986) as they require less bending of fibers. To each of these ends, a 2-inch-long hexagonal nipple (Cajon) connection was attached. The internal surface of the nipple was threaded in order to increase the metal-resin (epoxy or polyurethane resin was used for potting the fibers) bond strength.

The permeator assembly was thoroughly cleaned respectively with a soap solution, an aqueous sulphuric acid solution and water before the fiber bundle was inserted in it. The shell was completely immersed in water and the fiber bundle was gently pulled through the shell assembly by using a cotton thread

FIGURE 3-1
PHOTOGRAPH OF TWO SEPARATE MATS WITH BOTH
THE ENDS POTTED IN THE HEXAGONAL LONG NIPPLE

FIGURE 3-2
PHOTOGRAPH OF INTEGRATED MAT (SEPARATED AT
BOTH ENDS) TIED WITH COTTON THREADS

FIGURE 3-3
PHOTOGRAPH SHOWING END FITTINGS OF PERMEATOR #5

tied at one end of the bundle. Once the bundle was through at both the ends, two sets of fibers were separated and each set was then introduced through one of the hexagonal nipple connections. The whole assembly is shown in Figure 3-4. The assembly was air dried. Before the assembly was ready for potting, a tygon tube was slid over each fiber bundle end and attached to the hexagonal nipple by using a hose clamp. The other end of the tygon tube was connected with a polypropylene Y-connection. The fiber bundle was taken out through one arm of the Y-connection; the other arm was used to pour the resin mixture. The tygon tube was then given U-shape and clamped in that position. The arrangement is shown in Figure 3-5. The polyurethane resin mixture prepared with a 58:42 ratio of Polycin 1670 to Vorite 1701 (Cascchem Inc., Bayonne, NJ) was then poured into the U-tube through the free arm of the Y-connection. The resin was poured till the polyurethane level in the permeator end was raised to the middle of the nipple. Two arms of a Y were potted at a time. After 24 hours the fiber bundle at the end of the nipple was exposed by cutting off the polyurethane resin with a sharp knife. Seven more days were required for the complete curing of the resin. The configuration of such a permeator is shown in Figure 3-6.

The ends of permeators #8 and #9 were potted with epoxy resin (resin: C4; activator: D; ratio: 4:1; Beacon Chemical Co., Mt. Vernon, NY) instead of polyurethane. The potting technique was different from all other small-scale permeators. Epoxy resin was added through an opening made on the body of each Y-fitting. At the end of permeator construction, both the openings were plugged.

FABRICATION OF LARGE-SCALE HFCLM PERMEATORS

Three large-scale HFCLM permeators (#10, #11 and #12) had been built for large-scale gas purification studies. Each permeator contained a total of 7008, X-10 Celgard hollow fibers, divided equally between the feed and sweep sides. The fiber inside and outside diameters were 100 micron and 150 micron, respectively. The effective permeation lengths for permeators #10, #11 and #12 were 26, 24.5 and 24.5 inches, respectively.

The fiber mat preparation procedure for large-scale HFCLM permeators was somewhat different. A plexiglass sheet (size: 42"x21"x1/4") was mounted on an

FIGURE 3-4
PHOTOGRAPH OF A PERMEATOR WITH TWO SETS OF FIBER
TAKEN OUT THROUGH THE END FITTINGS

FIGURE 3-5
SCHEMATIC OF POTTING THE END OF A PERMEATOR
BY U-TUBE METHOD

FIGURE 3-6
SCHEMATIC OF HFCLM PERMEATOR ASSEMBLY WITH
TEFLON PIPE AND Y-FITTINGS AT THE END (PERMEATOR #5 TO #8)

electrically driven motor with proper connections. (The connection was made in the middle of the plexiglass piece.) It was wrapped twice with a polyethylene sheet to cover sharp edges at the ends. Celgard hollow fibers from a spool were then wound around the plexiglass sheet by rotating it slowly by hand. The fiber spool was kept away from the plexiglass/gear box arrangement and was allowed to rotate on a circular shaft. Distilled water was occasionally sprayed over the fibers for easy handling. Finally, a structure was created in which two layers of fibers remained at each side of the plexiglass sheet. One layer of fibers would be used as feed fibers, whereas the other layer of fibers would serve as sweep fibers. The polyethylene sheet along with the fibers were separated from the plexiglass by gently pulling the PE sheet from both ends. Four cotton threads were inserted (for permeator #10) in between the two layers of fibers. (For permeators #11 and #12, the cotton threads were placed and secured by means of several strips of scotch tapes on top of the polyethylene sheet at the beginning of the mat preparation procedure.) The threads were tied loosely at the ends of each fiber layer. The polyethylene sheet was then removed very carefully. At this point, one layer of fibers remained on top of the other layer. The four cotton threads were then tied very tightly and the layers were separated by cutting the fibers with a pair of scissors. The fibers were then rolled gently and slowly starting from the middle to form a 42-inch-long bundle of about 7000 fibers, keeping the four ends separated. Cotton threads were tied loosely to keep the fibers together.

A 2-ft.-long, 1-inch schedule 40 stainless steel pipe was used as the permeator shell. An epoxy mixture (C4-D) was applied to the outside surface of a teflon hollow rod (ID: 3/4 inch; OD: 1 inch), which was inserted into the stainless steel shell. After complete curing of the epoxy, the pipe was fitted with a nylon connection at each end (except for permeator #11). This connection was made in our machine shop from a 2-inch-thick nylon block. It had 3 large (size: 1 inch) openings in the form of a 'Y' and two small (size: 1/4 inch) openings. The central opening was attached to the stainless steel pipe, whereas the other two openings were connected to two hexagonal nipples, needed to separate the two sets of fibers. One of the small openings was used as the shell liquid port and the other one was plugged. For permeator #11, one SS 1-inch cross connection was connected to each end of the pipe. Two openings of the cross were fitted with two hexagonal nipples. The other opening would be

connected to the membrane liquid reservoir line.

The bundle was then inserted in the shell. Two sets of fibers were separated at the ends, and each set was then introduced through one of the hexagonal nipple connections. The whole operation was carried out keeping the bundle and the shell under water. To pot the fibers, a base sheet was first prepared on the hexagonal nipple using A-2 epoxy (Beacon Chemical Co., Mt. Vernon, NY). A second layer of epoxy (C4-D) was then poured on top of the A-2 epoxy using the 1/4-inch opening of the nylon connection. The curing procedure was carried out under centrifugal force i.e., the permeator was allowed to rotate on a vertical axis at high speed. The process ensured that the space between the adjacent fibers was filled with the epoxy resin. The resin was allowed to harden for 24 hours at room temperature. The procedure was repeated for all four ends. Figure 3-7 shows the three permeators.

PERMEATOR TESTING UNDER STATIC PRESSURE

Before a new permeator was used in the gas purification loop, it was necessary to test it for any leak which could be either in the tube sheet (made of either polyurethane or epoxy resin) due to incomplete wetting of the fiber by the resin or due to a defect or defects on the fiber surface or wall. Leak testing was done in the following manner.

The permeator shell was filled with distilled water and the shell side was pressurized by a N₂ cylinder, keeping the other shell side port completely closed. The pressure was increased slowly to 50 psig in steps of 10 psig. Observations were made at each pressure level for any sign of water coming out through the tube sides. Finally, the pressure was maintained at 50 psig and the permeator was checked for any further leakage of water through the tube sides. This type of test was carried out for all the permeators. As expected, the larger diameter fibers in the permeators #6 and #7 leaked more compared to the smaller diameter fibers. Generally, the leakage rate was small in all permeators; permeator #8 had the least leakage rate among the small-scale permeators.

Static pressure testing of large-scale permeators was normally carried out

FIGURE 3-7
PHOTOGRAPH OF THREE LARGE PERMEATORS (#10, #11 AND #12)

without removing the extra length of fibers from the tube-sheet. When tested for leaks, Permeator #12 was found to be leaking severely through one of the tube-sheets (90° end of a Cross) even at a low pressure of 5 psig. The permeator was allowed to dry thoroughly under vacuum and another layer of epoxy resin was applied through the shell liquid opening. The permeator was tested again and no improvement was seen. After drying the permeator, a hexagonal nipple with a coupler was attached to the leaky tube-sheet end and epoxy resin was poured from the top onto the extra length of fibers. The resin was allowed to harden for 24 hours and the permeator was tested again up to a pressure level of 50 psig. No leakage of water was noticed this time. The extra length of fibers from the other three ends were then removed by cutting them off with a sharp blade.

DESCRIPTION OF PURIFICATION LOOP FOR VARIOUS MODES IN SMALL-SCALE OPERATION

A photograph of the experimental setup used in this work is shown in Figure 3-8. The setup consisted mainly of three sections: feed line, sweep or permeate line and a membrane liquid supply line all tied to the HFCLM permeator. The permeator was maintained at 25°C by completely immersing it in a constant temperature water bath (CTB). The water circulation and temperature control were assured by a constant temperature circulator (Haake Inc., Saddlebrook, NJ; model NK 22). Only the sweep section was modified whereas the other two sections essentially remained unaltered in different modes of operation. All pieces of equipment in the setup were interconnected with either 1/4-inch stainless steel tube or 1/4-inch thickwalled polypropylene tubing. A primary standard gas mixture cylinder (Matheson, East Rutherford, NJ) containing CO₂ and N₂ or CO₂ and CH₄ was used as feed gas and pure helium or nitrogen was used as sweep gas. Shell liquid was pressurized by pure helium gas in all experiments.

SWEEP GAS MODE

The setup is described schematically in Figure 3-9. Feed line consisted of an oil filter, OF (one foot long, 1/2 inch stainless steel pipe, packed with glass wool), a feed humidifier, FH (a 20 liter stainless steel vessel, Millipore Corporation, Bedford, MA; equipped with a small pressure gauge of range,

FIGURE 3-8
PHOTOGRAPH OF THE PURIFICATION LOOP WITH THE PERMEATOR
IMMERSED IN THE CONSTANT TEMPERATURE BATH

BPR - BACK PRESSURE REGULATOR
 BV - BALL VALVE
 CPR - CYLINDER PRESSURE REGULATOR
 CTB - CONSTANT TEMPERATURE BATH
 CV - CHECK VALVE
 FH - FEED HUMIDIFIER
 FMC - FEED MIXTURE CYLINDER
 FT - FLOW TRANSDUCER
 FTC - FLOW TRANSDUCER CONTROLLER
 GV - GATE VALVE

HTP - HUMIDITY/TEMPERATURE PROBE
 LPGC - LIQUID PRESSURIZING GAS CYLINDER
 LST - LIQUID STORAGE TANK
 LT - LIQUID TRAP
 MT - MOISTURE TRAP
 OF - OIL FILTER
 PG - PRESSURE GAUGE
 RM - ROTAMETER
 SGC - SWEEP GAS CYLINDER
 SH - SWEEP HUMIDIFIER

FIGURE 3-9
 SCHEMATIC OF THE PURIFICATION LOOP FOR
 SWEEP GAS MODE OF OPERATION

0 - 160 psig and a safety valve), a humidity-temperature probe, HTP (Vaisala Inc., Woburn, MA; model HMP 32UT), an electronic mass flow transducer controller, FTC (Matheson model 8141-0452; range, 0 - 500 sccm), a Heise pressure gauge (Dresser Industries, Newton, CT; range, 0 - 250 psig). The humidity and the temperature of the feed gas stream coming out of FH were next monitored by HTP which was mounted in a stainless steel cylindrical cell connected to the gas line. The flow rate of the humidified feed gas was controlled and measured by FTC. A check valve, CV, was provided to prevent accidental injection of liquid from the permeator into the electronic flow controller. A three-way ball valve, located after the check valve, enabled the feed stream to bypass the permeator.

The purified feed gas stream from the permeator was passed successively through a liquid trap, LT, a pressure gauge (Matheson; range, 0 - 200 psig), a moisture trap column, MT, and a three-way bypass ball valve. The liquid trap was nothing but a three-inch-long 1/2-inch brass pipe. It was essentially a vertically located tee with the gas coming in at the branch line and going out through the top while liquid droplets collected at the closed bottom end. This device prevented carryover of the liquid droplets which appeared at the permeator tube sheet (from condensation or fiber leakage through the damaged fibers of the permeator, or both).

Moisture from the purified feed gas stream was eliminated by a moisture trap MT (Drierite Column Model #L68GP; W. A. Hammond Drierite Co., Xenia, OH), prior to the measurement of the flow rate by either a Fisher and Porter rotameter, RM (Phillips Co., South Hackensack, NJ; model 10 A 3555 AY) or by a Matheson electronic mass flow transducer (model 8141 - 0452; range, 0 - 500 sccm) connected in parallel. However, only the transducer was used for accurate measurement of the purified feed gas flow rate. The gas stream was next channelled respectively through a Fairchild back pressure regulator, BPR (Epec Sales, Towaco, NJ; range, 2 - 150 psi) to control the pressure of the feed gas stream and a check valve.

The composition of the purified feed gas stream emerging from the check valve was measured periodically by a gas chromatograph. A four-way switching ball valve was utilized to this end beyond the check valve.

The nature of the instrumentation in the sweep gas line was essentially identical to that in the feed gas line with the following exceptions. To accommodate higher sweep gas flow rate, two 20 liter Millipore stainless steel vessels, SH, were connected in series for humidification of the sweep gas stream. Moreover, an electronic mass flow transducer and transducer - controller, FTC, of higher flow rate ranges (Matheson model 8141 - 0413; range, 0 - 1000 sccm) were used to measure and control the sweep side gas flow rate. A Matheson test gauge (range, 0 - 100 psig) and a Heise compound gauge (range, 30 inch vac - 15 psig) were used to measure the pressure at the sweep gas inlet and outlet locations of the permeator, respectively. The Fairchild back pressure regulator, used to control the sweep stream pressure, had a range of 0 - 10 psi.

The permeator shell side inlet was connected to the membrane liquid storage tank, LST (a 10 liter Millipore stainless steel vessel), through a check valve and an on-off ball valve. The liquid storage tank was pressurized by a gas cylinder, LPGC, through an oil filter and a gate valve. The pressure of the liquid line connecting LST to the permeator was indicated by a Matheson test gauge (range, 0 -200 psig). This pressure was always maintained at a level higher than those of both the feed and the sweep gas streams. The pressure of the LST could be independently changed if necessary, by manipulating the on-off ball valve. This was particularly useful during start-up and shutdown of the system. The shell side outlet was kept closed by a gate valve. It was opened to drain the membrane liquid from the permeator when the system was shut down and the permeator was not operational.

The gas flow rate readings of the four transducers were monitored centrally by a Matheson digital readout and control module (model 8249). The same module was used to set and control the gas flow rates at the permeator inlets. The humidity and temperature of both gas streams entering the permeator were displayed on a digital indicator (Vaisala Inc., Woburn, MA; model HMI 32). The indicator utilized a HMS 13 probe selector to measure the humidity and temperature of one gas stream at a time.

For purification runs with 40% CO₂-60% CH₄ feed gas mixtures, additional steps

were taken. The complete purification loop was enclosed with a polyethylene cover with an opening at the top which was connected to the exhaust hood. Inside this enclosed space was located a CH₄ detector (Model 462484, MSA Inc., Pitts., PA). Outside the cover, a similar detector was located. Both of them were connected to a control module (Model 465740, MSA Inc., Pitts., PA) and horn outside the cover. Additionally, a N₂ cylinder was provided to flush the feed gas line after a separation run was carried out.

CONVENTIONAL POLYMERIC MEMBRANE MODE

No modification of the purification loop was needed to operate the system in the conventional polymeric membrane mode. In the absence of a sweep gas, one end of the permeator (previously sweep inlet end) was kept closed; the three-way ball valve in the sweep gas inlet line was switched to the other direction so that it automatically closed that end. The schematic of the corresponding experimental loop is shown in Figure 3-10.

VACUUM MODE

To carry out purification studies in the vacuum mode, a few modifications were made. The modified schematic of the same is shown in Figure 3-11. Note that, no change was made in the feed gas and membrane liquid supply lines. In the absence of a sweep gas, one end of the permeator (previously inlet end) was kept closed. The pressure of the closed end was measured by a Heise vacuum gauge. A Heise compound gauge (range 30 inch vac - 15 psig) was used to monitor the pressure at the permeate outlet through which vacuum had been pulled. Duo-seal two-stage rotary vane vacuum pump (Model #1400, Sargent-Welch Scientific Co., Skokie, IL) was used to create and maintain the vacuum. Moisture from the permeate stream was eliminated by a Drierite Column Model # 168GP (W. A. Hammond Drierite Co., Xenia, OH) before the vacuum pump. An oil filter, packed with glass wool and Drierite, was provided after the vacuum pump exhaust line to eliminate the oil and moisture from the permeate stream. The permeate line was connected through a four-way switching ball valve to the gas chromatograph (GC) to measure the composition of the permeate stream periodically. The permeate flow rate was measured by a soap bubble flowmeter after the GC.

HTP - HUMIDITY/TEMPERATURE PROBE
LPGC - LIQUID PRESSURIZING GAS CYLINDER
LST - LIQUID STORAGE TANK
LT - LIQUID TRAP
MT - MOISTURE TRAP
OF - OIL FILTER
PG - PRESSURE GAUGE
RM - ROTAMETER

FIGURE 3-10
SCHEMATIC OF THE PURIFICATION LOOP FOR CONVENTIONAL
POLYMERIC MEMBRANE MODE OF OPERATION

HTP - HUMIDITY/TEMPERATURE PROBE

LPGC - LIQUID PRESSURIZING GAS CYLINDER

LST - LIQUID STORAGE TANK

LT - LIQUID TRAP

MT - MOISTURE TRAP

QF - OIL FILTER

PG - PRESSURE GAUGE

RM - ROTAMETER

VP - VACUUM PUMP

For purification runs using CO_2 - CH_4 gas mixtures as feed, an explosion-proof single-stage vacuum pump (Model #1410W-01, Sargent-Welch Scientific Co., Skokie, IL) was used. The permeate outlet gas at the vacuum pump outlet was allowed to flow through the oil filter-cum-Drierite column to the four-way switching valve and then it was sent either to the GC or to the exhaust hood. Permeate gas flow rate was measured by a soap bubble flowmeter kept under the exhaust hood. The outlet from GC was also connected to the exhaust hood. At the end of an experiment, feed gas was switched to nitrogen gas to flush both feed line as well as the permeate line.

SWEEP WATER MODE

Purification studies in the sweep water mode required some modifications. No change was made in the feed gas and the membrane liquid supply line. Two large (80 liter) plastic vessels were used to store distilled water. A Cole Parmer Gear Pump (Model #7144-04) with a Variable Speed Controller (range, 165 - 3600 rpm) was used to circulate distilled water through the sweep fibers. Pressures at the sweep water inlet and outlet ends were measured by 2-1/2-inch-diameter Matheson pressure gauges (range: 0 - 60 psig). The modified schematic of the loop is shown in Figure 3-12.

DESCRIPTION OF THE LARGER PURIFICATION LOOP

The experimental setup used for long-term purification of model biogas mixture is described schematically in Figure 3-13. The instrumentations in the setup were supported on a laboratory flexframe structure. The interconnections between various equipment were either by 1/4-inch stainless steel tube or by 1/4-inch thick-walled polypropylene tubing.

Although the plumbing in this purification loop was more complex than the one we described earlier, it essentially contained three different flow lines, e.g., feed gas line, sweep gas line and membrane liquid storage line. Three CO_2 gas cylinders and three CH_4 (or N_2) cylinders, connected by two separate manifolds ensured a constant supply of gases. Each gas stream was sent through an oil filter (1/2-inch stainless steel pipe, packed with glass wool) to remove

BPR - BACK PRESSURE REGULATOR
 BV - BALL VALVE
 CPR - CYLINDER PRESSURE REGULATOR
 CTB - CONSTANT TEMPERATURE BATH
 CV - CHECK VALVE
 FH - FEED HUMIDIFIER
 FMC - FEED MIXTURE CYLINDER
 FT - FLOW TRANSDUCER
 FTC - FLOW TRANSDUCER CONTROLLER
 GV - GATE VALVE

HTP - HUMIDITY/TEMPERATURE PROBE
 LPGC - LIQUID PRESSURIZING GAS CYLINDER
 LST - LIQUID STORAGE TANK
 LT - LIQUID TRAP
 MT - MOISTURE TRAP
 OF - OIL FILTER
 PG - PRESSURE GAUGE
 RM - ROTAMETER
 WP - WATER PUMP
 WST - WATER STORAGE TANK

FIGURE 3-12
 SCHEMATIC OF THE PURIFICATION LOOP FOR
 SWEEP WATER MODE OF OPERATION

FIGURE 3-13
SCHEMATIC OF THE LARGE-SCALE PURIFICATION LOOP

oil droplets, if any. The filtered gas streams were connected to two electronic flow transducer - controllers (transducer model no. 8102; controller model no. 8202) of a Matheson Dyna-blender (Model No. 8250). This blender allowed one to prepare a gas mixture of a specific composition at a given flow rate. Thus, model biogas feed mixture was prepared in situ by blending CO₂ and CH₄ (or N₂) gases.

The blended gas mixture was sent through a feed humidifier, a 21-inch-long hollow-fiber membrane contactor, made in our laboratory for this particular project. It contained 6000 Celgard polypropylene hollow fibers. The structure of this humidifier was similar to that of a shell-and-tube type heat exchanger. The feed gas was passed through the tube-side and the shell was completely filled with water. To ensure constant supply of water, a water storage tank was attached to the shell-side of the humidifier. The pressure of the water tank was maintained at a higher level than that of the feed gas pressure by a gas cylinder, connected to the other end of the tank. An indicator was also provided to identify the water level in the storage tank. The trap located after the humidifier captured water droplets which appeared due to condensation and/or leakage through the damaged fibers. The humidifier bypass line allowed one to switch instantly from humidified gas mixture to partially humidified or completely dry gas mixture.

The humidity and the temperature of the feed gas stream were monitored by a probe (model 32UT, Vaisala Inc., Woburn, MA), mounted in a Teflon cell connected to the gas line. The check valve prevented any accidental flow in the opposite direction. A three-way ball valve enabled the feed stream to bypass the permeator. The feed stream pressure at the permeator inlet was indicated by a pressure gauge (0-200 psig, Matheson, E. Rutherford, NJ). The purified gas stream from the permeator was passed through a liquid trap. A pressure gauge indicated the outlet gas pressure. The humidity and temperature of the purified gas stream were measured by another humidity probe. Moisture from the purified gas stream was eliminated by a Drierite column (W.A. Hammond Drierite Co., Xenia, OH) prior to the measurement of its flow rate. The flow rate was measured by an electronic mass flow-transducer (model No. 8202; Matheson). The gas stream was then passed through a Fairchild back pressure regulator (Epec Sales, Towaco, NJ) and a check valve. The back pressure

regulator was used to control the pressure of the feed gas stream. The composition of the purified gas stream was measured periodically by a gas chromatograph.

The instrumentations in the sweep gas line were essentially similar to those of the feed gas line with the following exceptions. A pure gas (N_2 or He) was introduced as a sweep gas, therefore, only one gas manifold containing three cylinders was used. The sweep line water storage tank for humidification was pressurized by the sweep gas itself; no separate gas cylinder was necessary here.

The permeator shell-side inlet was connected to a membrane liquid storage tank through a check valve and an on-off ball valve. The liquid storage tank was pressurized by a gas cylinder through an oil filter and a gate valve. The pressure of this liquid line was indicated by a Matheson test gauge. This pressure was always maintained at a level higher than those of both the feed and sweep gas streams. The shell-side outlet was kept closed by a gate valve. This particular valve was used to drain the membrane liquid from the permeator.

The permeator shell was maintained at a desired temperature level by completely immersing it in a water bath. It was made of galvanized iron with insulations on all five sides. The inner surface of the bath was painted with a special polyurethane and epoxy to minimize corrosion by water. The water temperature was maintained by a constant temperature circulator (Haake Inc., Saddle Brook, NJ, model NK 22).

The gas flow rate readings of the transducers were monitored centrally by a Matheson digital readout and control module (model 8209). The humidity and temperature of all gas streams were displayed on a digital indicator (Vaisala Inc., Woburn, MA; model HMI 32). The indicator utilized a HMS 13 probe selector to measure the humidity and temperature of one gas stream at a time. A photograph of the experimental setup is shown in Figure 3-14.

EXPERIMENTAL PROCEDURE

In both cases, the entire flow loop was occasionally tested for leak by

FIGURE 3-14
PHOTOGRAPH OF THE LARGE-SCALE PURIFICATION LOOP

pressurizing the system with N_2 gas. Dry gas was used in all the experiments where water acted as liquid membrane. Whenever aqueous solution was used as membrane, humidified feed gas was used. For sweep gas mode of operation with such membranes, sweep gas was also humidified. However, dry feed gas was used in the sweep water mode experiments.

To start the system, the permeator shell side was first filled with the membrane liquid by manipulating the on/off valve, located on the liquid storage tank. The latter was initially maintained at about 10 to 15 psig. The feed and sweep gas flow were then initiated, keeping the pressure in the feed and the sweep gas line lower than the storage liquid pressure. A helium cylinder was always used to pressurize the membrane storage tank. The pressure in either flow line was determined primarily by the back pressure regulator setting. The membrane liquid storage tank pressure was also increased slowly to the desired level. The feed and sweep gas flow rates were then set at the desired values. Finally the feed inlet and sweep outlet pressures were set at particular values by manipulating the back pressure regulators. Measurements of the gas flow rates, pressures, humidities, temperatures and outlet gas compositions were made at regular interval.

To shut down the system, the valve connecting the shell liquid storage tank with the permeator was first turned off and the gas pressure as well as the flow rates in each line (sweep gas mode) were slowly reduced. The liquid pressure in the permeator shell was released by opening the shell side gate valve.

The experimental procedure under conventional polymeric membrane mode was similar to that of sweep gas mode with the exception that no sweep gas was used. One end of the permeator (previously sweep inlet end) was closed by switching the three-way ball valve. Thus the permeated gas was only flowing through the permeate fibers countercurrent to the feed gas. Permeate flowrate was also checked by the soap-bubble flow meter in all the experiments.

All experiments under vacuum mode of operation needed thorough leak testing of the lines under vacuum. The vacuum pump was turned on and the valve between the inlet of vacuum pump and the Drierite column was kept open. Once the desired

vacuum was achieved, the valve was closed and the system was kept in that condition for about two hours to check if there was any drop in vacuum. The experiment was started when the system was found to be leak proof.

The pressurization step was similar to that of sweep gas mode of operation, but the vacuum was applied to the system while the shell liquid pressure was at about 15 psig. Gradually, both shell liquid pressure and the feed side gas pressure were raised to the desired level with proper setting of feed gas flow rate. Measurement procedures were similar. Shut down procedure was also similar but at first the vacuum pump was disconnected from the system. However, in the case of $\text{CO}_2\text{-CH}_4$ gas mixture as feed, experiment was continued by switching the feed gas to N_2 and continuously the feed and the permeate streams were monitored by GC for the presence of CH_4 till there was essentially no CH_4 in either stream.

When the system was operated in sweep water mode, the procedure undertaken was exactly similar to those used in the case of sweep gas mode of operation. However, the flow of sweep water was started when shell liquid pressure as well as feed side pressure and flow rate were set. The flow rate of water was measured at the outlet by a measuring cylinder and stop watch.

MEASUREMENT OF GAS PERMEABILITY THROUGH THE LIQUID MEMBRANE

The measurement of permeability of CH_4 through water was carried out using the immobilized liquid membrane (ILM) technique. The same technique was adopted to measure the permeabilities of N_2 and CO_2 through aqueous solution of 20 wt% DEA at different partial pressures of CO_2 .

Permeation rate of any gas species through a liquid membrane was determined by the sweep gas method (Bhave and Sirkar, 1986). Feed gas (pure or a mixture) was first completely humidified and passed over a film containing water or aqueous solution in the test cell at a given pressure (usually greater than atmospheric but not necessarily). On the other side of the film, a completely humidified helium sweep gas stream was passed at essentially atmospheric pressure and a known flow rate. This flow rate and the rates of permeation of the components of the gas mixture were such that the permeated species were not

present in the sweep gas at concentrations higher than, say 2-3 mole percent. This sweep gas stream was then analyzed by a gas chromatograph. The permeation rate was obtained easily; knowing the sweep helium flow rate and the permeated gas species content of this stream is equivalent to knowing the flow rate of that species, the latter coming about strictly due to permeation.

The available experimental setup for the measurement of gas permeability through an aqueous liquid membrane immobilized in a hydrophobic microporous film is shown in Figure 3-15. The setup and the procedure are described below.

Pure water or the aqueous solution was immobilized in the pores of a hydrophobic microporous polypropylene film Celgard 2400 (2.54×10^{-3} cm thick with a porosity of 0.38 and average effective pore size of 0.02 micron) by the exchange technique of Bhave and Sirkar (1986). The exchanged Celgard 2400 film with a nominal diameter of 5.1 cm was placed in the test cell. The Celgard film was supported by two thick Accurel polypropylene films (each 0.010 cm thick and 3.5 cm in diameter having an average pore size of 0.2 microns from Armak, Chicago, Illinois) and a porous, 6-mil-thick, fine circular stainless steel screen having the same nominal diameter as Accurel films (Pall Trinity Micro Corporation, Cortland, NY). The membrane was sealed by a set of O-rings measuring 4.4 cm and 5.7 cm. To be especially noted here is that the pore size of Accurel is one order of magnitude larger than the pore size of Celgard. Thus, Accurel films were used simply as a backing to protect the Celgard film from any accidental sharp edges of the stainless steel screen employed to support the high pressure difference across the ILM. The area available for gas permeation was 13.19 cm^2 . The test cell was immersed in a constant temperature bath (HAAKE constant temperature immersion circulator, Model D1) obtained from Fisher Scientific, Springfield, N.J.

The placing of this film in the test cell (TC) was preceded by adjustment of the desired flow rates of humidified streams of feed gas and the sweep helium gas, respectively. This was done with the help of Matheson Digital transducers and control valves FTC-s shown in Figure 3-15. In order to ensure complete humidification of both the feed and sweep gas streams before they enter the test cell, the humidification process was carried out for each stream for at least 12 hours in two high-pressure Hoke sample cylinders before the start of

FIGURE 3-15
 SCHEMATIC OF THE EXPERIMENTAL SETUP FOR GAS
 PERMEABILITY MEASUREMENT THROUGH AN IMMOBILIZED
 LIQUID MEMBRANE

each permeation experiment. Each humidifier vessel was filled with about 400 cc of distilled water. Additional water was added from time to time to compensate for the loss during humidification of the gas streams. The gas space volume above water in each humidifier (FH-s, SH-s) was around 100 cc. With about 10-15 cc/min flow rate of either the feed stream or the sweep stream, the humidified gas in two successive reservoirs was sufficient to ensure an uninterrupted supply of completely humidified gas for a long time.

Further, in order to verify the extent of saturation of the sweep gas and the feed gas stream with respect to water vapor, the probes (HTP) of a high precision digital relative humidity/temperature measurement system (Model HS-2CHDT-2A, Thunder Scientific Corporation, Albuquerque, New Mexico) were located just before the cell inlets. The desired feed side pressure was next achieved by means of the back pressure regulator BPR. The sweep gas was always maintained at around 0.1 psig to prevent any possibility of surrounding air leaking into the system. The sweep gas samples were drawn into the Gas Chromatograph column through a gas sampling valve for analysis. Samples were drawn over regular intervals (e. g., 15-20 minutes) to determine the progress of the permeation experiment. To eliminate moisture in the sweep gas so that there is no long tailing in the TCD output, the sweep gas sample was passed through a moisture trap (MT) (essentially a column of Drierite) in the sweep line just before the gas sampling valve in the GC.

Initially, leak testing was carried out on the entire loop using nitrogen from a nitrogen cylinder (NC). The same nitrogen cylinder was also kept as standby for flushing the complete flow loop when a mixture containing CH_4 was utilized.

Since the flow rate of the sweep gas is quite important for the accurate determination of the permeability of any gas species, the sweep flow line after the GC was taken to an exhaust hood where the flow rate was measured using a soap bubble flow meter. The feed gas line was also connected to the exhaust hood after the back pressure regulator.

CALIBRATION AND ANALYSIS

The compositions of the purified feed gas stream and the sweep or permeate

outlet stream were measured by a Varian Gas Chromatograph (GC) (Varian Instruments, Palo Alto, CA;) with a thermal conductivity detector (TCD). Varian model 3700 GC was used in small-scale operation whereas model 3400 GC was used in large-scale operation. The response from the detector was recorded by a digital reporting integrator (Hewlett Packard, Paramus, NJ; model 3390 A or Varian model 4290). A six-foot-long 1/8-inch stainless steel Porapak N 80/100 mesh columns was used for separation of the gas mixture.

Since helium was used as a carrier gas, the thermal conductivity detector could not detect He. Feed and sweep outlet streams would contain CO_2 , N_2 and helium in varying proportions when helium was used as sweep gas and gas mixture containing CO_2 and N_2 was used as feed. Therefore, it was necessary to develop calibrations in terms of absolute areas of CO_2 and N_2 rather than area percent. The helium content in the samples could then be estimated by subtracting the combined CO_2 - N_2 percentage from 100. The calibration curves were developed for CO_2 , CH_4 and N_2 by utilizing primary standard gas mixtures and/or gas mixtures obtained by carefully controlled mixing of pure gases in different proportions using a modular Dyna-blender (Matheson, model 8250). A few sample calibration curves for Varian 3700 and 3400 GC are shown in Figures 3-16 and 3-17, respectively.

FIGURE 3-16
ABSOLUTE AREA CALIBRATION FOR CO_2 AND N_2
FOR VARIAN 3700 GC

FIGURE 3-17
ABSOLUTE AREA CALIBRATION FOR CO₂ AND CH₄ FOR VARIAN 3400 GC

Section 4

RESULTS AND DISCUSSION

Experimental data and numerical simulation results for biogas purification in HFCLM permeators are presented in this section. Results of each mode of operation (e.g., sweep gas, conventional, vacuum and sweep water) are discussed separately. The feed mixture compositions and other parameters, used in a given set of experimental studies, are clearly mentioned in each table.

ESTIMATION OF PURE COMPONENT GAS PERMEABILITIES THROUGH WATER

The permeability of a gas species, Q_i , through a pure water film may be estimated from the product of the diffusivity of the gas species through water, D_{iw} , and the solubility of the gas species in water, H_{iw} :

$$Q_i = D_{iw} \times H_{iw} \quad (4-1)$$

The diffusivity and the solubility values were obtained from a variety of sources cited in Table 4-1. Since all the experiments were carried out at 25°C, the permeability values of CO_2 , N_2 , He and CH_4 , reported in Table 4-1, were used for all the numerical simulations where water was used as liquid membrane.

Permeability of CH_4 was also determined experimentally by measuring the permeation rate of pure CH_4 through fully exchanged Celgard 2400 ILM film containing water as immobilized liquid membrane. The results, presented in Table 4-2, show that the permeability of CH_4 through pure water is more or less constant over the experimental range of pressure differences. These values are quite close to that obtained from the literature (Table 4-1).

ESTIMATION OF PURE COMPONENT GAS PERMEABILITIES THROUGH AQUEOUS SOLUTIONS OF DEA

Permeabilities of a nonreacting species (e.g., N_2 or He) through aqueous solutions of DEA were estimated from pure component permeation studies, in the absence of CO_2 gas, under conventional polymeric membrane mode in permeator #8.

Table 4-1

PERMEABILITIES OF PURE GASES THROUGH WATER AT
DIFFERENT TEMPERATURES

Temp °C	Gas	$D_{iw} \times 10^5$ cm ² /sec	$H_{iw} \times 10^4$	$Q_i \times 10^9$	$Q_i \times 10^{14}$
			$\frac{\text{scc(g)}}{\text{cc(w)-cm Hg}}$	$\frac{\text{scc-cm}}{\text{cm}^2\text{-s-cm Hg}}$	$\frac{\text{mole-m}}{\text{m}^2\text{-s-Pa}}$
15	CO ₂	1.4 ¹	133.2 ²	186.5	62.40
	N ₂	2.2 ³	2.22 ²	4.88	1.63
	He	6.2 ³	1.30 ²	8.06	2.69
	CH ₄	2.15 ³	4.87 ²	10.47	3.50
25	CO ₂	1.92 ¹	109.3 ²	210.0	70.27
	N ₂	3.0 ³	1.86 ²	5.58	1.86
	He	7.4 ³	1.316 ²	9.74	3.26
	CH ₄	2.7 ³	3.97 ²	10.72	3.59
35	CO ₂	2.4 ¹	78.2 ²	187.7	62.81
	N ₂	3.9 ³	1.67 ²	6.51	2.18
	He	8.4 ³	1.34 ²	11.25	3.76
	CH ₄	3.6 ³	3.38 ²	12.17	4.07

- References :
1. Thomas and Adams (1965)
 2. Perry and Chilton (1973)
 3. Wise and Houghton (1966)

Table 4-2

PERMEABILITY OF CH₄ THROUGH FULLY EXCHANGED
CELGARD 2400 ILM⁴ CONTAINING WATER AT 25°C

RUN #	Pressure Difference* cm Hg	Tortuosity τ^+	$Q_{CH_4} \times 10^9$
			$\frac{scc-cm}{cm^2-s-cm\ Hg}$
1	126.8	3.77	8.71
2	152.5	3.81	9.24
3	178.2	3.84	8.59
4	203.8	3.87	9.69
5	229.6	3.92	9.07
6	280.9	4.07	9.67

* Pressure Difference = Feed Pressure (pure CH₄) - Partial Pressure of CH₄ in Permeate

+ Tortuosity values were taken from Bhawe and Sirkar (1986)

The shell liquid was pressurized by a helium gas cylinder in all experiments. The differential equations (2-91) to (2-94) were solved simultaneously for different values of gas permeability. The correct species permeability should describe the observed pure component permeation behavior. The experimental data and the results from numerical analysis for N_2 and He are presented in Tables 4-3 and 4-4, respectively. In all the calculations described above, the effective membrane thickness in permeator #8 was considered to be 0.00485 inch. This particular value was determined from pure CO_2 permeation studies through water as liquid membrane described later.

Permeability of a nonreacting species can also be estimated from the product of diffusivity and solubility through the solution. Sada et al. (1978) have studied the diffusivity and solubility of gases in aqueous solutions of amines. The diffusivity values of different gas species were estimated in two ways. In the first method, the variations of diffusivity of N_2O in aqueous solution of DEA measured by Sada et al. (1978) were used. Diffusivity value was correlated with the concentration of DEA solution by the following equation :

$$(D_{iAm}/D_{iw}) = (D_{Am}/D_w)_{N_2O} = 1.0 - 0.11352 C_T \quad (4-2)$$

where C_T is the concentration of DEA in mole/l.

In the second method, diffusivity value was estimated by Stokes-Einstein equation using the viscosity values measured by Sada et al. (1978):

$$(D_{iAm}/D_{iw}) = (\mu_{Am}/\mu_w)^{-1} \quad (4-3)$$

Similarly, solubility value of N_2O measured by Sada et al. (1977) was correlated by the following equation (Blanc and Demarais, 1984)

$$\ln (H_{iAm}/H_{iw}) = 1.0406 \times 10^{-4} + 6.8433 \times 10^{-3} C_T + 1.33633 \times 10^{-2} C_T^2 - 1.1549 \times 10^{-3} C_T^3 \quad (4-4)$$

Table 4-5 shows the estimated values and averaged experimental values (obtained from Tables 4-3 & 4-4). Permeability of CH_4 was not determined using pure component permeation method because of safety reasons. Higher experimental

Table 4-3

SIMULATION RESULTS AND EXPERIMENTAL DATA OF PURE NITROGEN PERMEATION RUN
WITH DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

$Q_{N_2} \times 10^9$ scc cm	WT% DEA in Water	Feed Side Flow Rate scc/min inlet	Permeate Flow Rate scc/min outlet	Feed Side Pressure psig inlet/outlet	Permeate Side Pressure psig inlet/outlet
<u>cm²-s-cm Hg</u>					
Data	10	250.0 300.0	3.25 3.22	44.5/43.2 44.75/43.2	0.7/0.1 0.5/0.1
Simulation					
4.86		250.0	3.25	44.5/42.7	0.14/0.1
4.805		300.0	3.22	44.75/42.7	0.14/0.1
Data	20	150.0 200.0	2.262 2.28	43.2/42.0 43.5/42.0	0.6/0.1 0.6/0.1
Simulation					
3.46		150.0	2.262	43.2/42.15	0.13/0.1
3.475		200.0	2.28	43.5/42.1	0.13/0.1
Data	30	150.0 200.0	1.782 1.726	44.75/43.6 44.8/43.2	0.5/0.1 0.5/0.1
Simulation					
2.628		150.0	1.782	44.75/43.73	0.12/0.1
2.553		200.0	1.726	44.8/43.43	0.12/0.1

Feed: 99.99% N₂; Shell Press.: 50 psig; Bath Temp.: 25°C; 100% Humidified Feed Gas;
Membrane Thickness Used = 0.00485 inch

Table 4-4

SIMULATION RESULTS AND EXPERIMENTAL DATA OF PURE HELIUM PERMEATION RUN
WITH DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

$Q_{He} \times 10^9$ scc cm cm ² -s-cm Hg	WT% DEA in Water	Feed Side Flow Rate scc/min inlet	Permeate Flow Rate scc/min outlet	Feed Side Pressure psig inlet/outlet	Permeate Side Pressure psig inlet/outlet
Data	10	150.0 200.0	6.05 6.15	44.75/43.4 44.9/43.0	1.0/0.2 1.0/0.2
Simulation					
8.965		150.0	6.05	44.75/43.61	0.29/0.2
9.125		200.0	6.15	44.9/43.5	0.29/0.2
Data	20	150.0 300.0	6.112 6.693	44.5/43.2 44.8/43.0	0.5/0.1 0.5/0.1
Simulation					
9.09		150.0	6.112	44.5/43.3	0.2/0.1
10.02		300.0	6.693	44.8/42.5	0.2/0.1
Data	30	150.0 200.0 300.0	5.525 5.523 5.695	43.5/42.2 45.0/43.3 44.9/42.5	0.6/0.1 0.8/0.1 0.7/0.1
Simulation					
8.405		150.0	5.525	43.5/42.33	0.19/0.1
8.155		200.0	5.523	45.0/43.3	0.19/0.1
8.505		300.0	5.689	44.9/42.57	0.19/0.1

Feed: 99.99% He; Shell Press.: 50 psig; Bath Temp.: 25°C; 100% Humidified Feed Gas;
Membrane Thickness Used : 0.00485 inch

Table 4-5

ESTIMATED PERMEABILITY OF GASES THROUGH
AQUEOUS SOLUTION OF DEA AT 25°C

Wt% DEA	C _T mole/l	GAS	$D_{iAm}^1 \times 10^5$ cm ² /sec	$D_{iAm}^2 \times 10^5$ cm ² /sec	$H_{iAm}^* \times 10^5$	$Q_{iAm}^1 \times 10^4$	$Q_{iAm}^2 \times 10^9$	$Q_{iAm}^+ \times 10^9$
10	0.96	N ₂	2.67	2.11	1.83	4.88	3.86	4.83
		He	6.59	5.21	1.29	8.52	6.72	9.05
		CH ₄	2.41	1.90	3.90	9.40	7.41	-
20	1.9429	N ₂	2.34	1.43	1.76	4.12	2.52	3.47
		He	5.77	3.52	1.24	7.15	4.36	9.52
		CH ₄	2.10	1.28	3.76	7.89	4.82	-
30	2.9486	N ₂	2.0	0.84	1.67	3.34	1.40	2.59
		He	4.92	2.07	1.18	5.81	2.44	8.36
		CH ₄	1.80	0.75	3.56	6.41	2.67	-

Q_i values are expressed in scc-cm/cm²-s-cm Hg*H_i values are expressed in scc/cc-cm Hg and calculated using Eq. 4-41 D_i¹ values are obtained from Eq. 4-22 D_i¹ values are obtained from Eq. 4-3

+ Average experimental values obtained from Table 4-3 and 4-4 respectively

value compared to estimated value for He could be explained by the fact that the size and the molecular weight of He are much smaller than those of N₂O; therefore, N₂O is not the right choice to predict the permeability of He. So, for all the numerical simulations, the experimental permeability values for He were used.

The measurement of permeability of CO₂ was carried out using the immobilized liquid membrane (ILM) technique. An independent measurement of tortuosity factor of Celgard 2400 support film was first made at different pressures using pure N₂ gas permeation through such a film having pure water in its pores. An average tortuosity value of 5 was obtained for the pressure range studied.

Table 4-6 indicates the permeation and separation behavior of CO₂-N₂ mixtures through fully exchanged Celgard ILM containing an aqueous 20 wt% DEA solution (it is reported later that 20 wt% DEA solution gave the best separation behavior in HFCLM permeator in the partial pressure range of CO₂ being studied). Two different gas mixtures containing 5% CO₂-95% N₂ and 25% CO₂-75% N₂ were used as feed. The total pressure of the feed mixture was kept between 231.14 cm Hg and 515.57 cm Hg. Note that, the partial pressure range of CO₂ covers the entire range studied for separation experiments in the HFCLM permeator. From the measured permeation rate of N₂ and CO₂, the permeability values of N₂ and CO₂ through 20 wt% DEA solution were calculated using the following relation:

$$Q_i = [R_i \times t_m \times \tau_m] / [\Delta P_i \times \epsilon_m \times A_m] \quad (4-5)$$

The nitrogen permeability value (1.75×10^{-9} scc-cm/cm²-s-cm Hg) obtained in this set of measurements is about half of that (3.4675×10^{-9} scc-cm/cm²-s-cm Hg) obtained earlier in our pure component permeation runs in the permeator #8 (Table 4-3). Note that pure component permeation runs were carried out in the absence of CO₂ gas. When CO₂ dissolves in the aqueous solution of DEA, the following overall reaction occurs:

It is possible that when CO₂ is present along with N₂, the N₂ permeability

Table 4-6

PERMEATION AND SEPARATION BEHAVIOR OF CO₂-N₂ MIXTURES THROUGH FULLY
EXCHANGED CELGARD ILM-S CONTAINING AQUEOUS 20 WT% DEA SOLUTIONS

Total Pressure cm Hg	ΔP_{N_2} cm Hg	ΔP_{CO_2} cm Hg	$R_{N_2} \times 10^3$ scc/sec	$R_{CO_2} \times 10^3$ scc/sec	$Q_{N_2} \times 10^9$	$Q_{CO_2} \times 10^9$	Separation Factor (Q_{CO_2}/Q_{N_2})
282.8	268.63	11.99	0.1826	2.2506	1.747	482.46	276.2
360.4	342.31	15.47	0.2294	2.2546	1.666	362.20	217.41
438.0	415.97	19.04	0.2680	2.2069	1.646	296.10	179.89
515.6	489.64	22.57	0.3165	2.2384	1.610	246.97	153.40
231.1	173.26	55.14	0.1323	3.7037	1.938	170.4	87.92
282.8	212.03	67.93	0.1557	3.9436	1.887	149.20	79.07
360.4	270.23	87.86	0.1906	4.684	1.753	132.54	75.61
438.0	328.39	107.23	0.2262	4.722	1.759	112.48	63.94
515.6	386.55	126.53	0.2707	4.948	1.744	97.40	55.85

ILM thickness = 2.54×10^{-3} cm; Temperature = 25°C; Flat film area = 13.19 cm²;
Tortuosity values corresponding to total pressure values are used for calculation
 Q_{N_2} and Q_{CO_2} values were in scc-cm/(cm² -s-cm Hg)

value reduces further due to the presence of other ions e.g., R_2NCOO^- and $R_2NH_2^+$ in the liquid membrane. Moreover, relative amounts of association among this polar intermediate further lowers the permeability (Donaldson and Nguyen, 1980). However, the estimated value of 2.52×10^{-9} scc-cm/cm²-s-cm Hg from Table 4-5 for N_2 lies in between the above two values. Thus it is expected that the values listed in the eighth column of this table for N_2 and CH_4 would be a better choice to analyze the actual separation data in HFCLM permeator.

The observed separation factors of CO_2 and N_2 through 20 wt% DEA solution at different partial pressures of CO_2 have been compared with the numerical simulation results based on the analysis discussed in Section 2 and presented in Table 4-7. Though the present model predicted the separation factors quite well as shown in Figure 4-1, the permeability values of CO_2 were always overpredicted (see Tables 4-6 and 4-7) to a great extent. This could be due to uncertainties in the estimation of other parameters, such as, diffusivity of amine, rate constants and reaction orders with respect to DEA which have considerable effects on the prediction (Donaldson and Nguyen, 1980). Experimental diffusivity of amine (Thomas and Furzer, 1962), measured in the absence of reaction, was used. The equilibrium constants K_{Am} and K_p at 20°C were obtained from Danckwerts and Sharma (1966), who reported that the values of the equilibrium constants are influenced substantially by the ionic strength of the solution; it is not generally possible to make accurate allowance for this. Therefore, those values were used for the present analysis. In addition, it should be remembered that other investigators have studied only the forward reaction in the absence of significant carbamate product which will have a noticable effect on all these parameters.

ESTIMATION OF EFFECTIVE MEMBRANE THICKNESS IN SMALL PERMEATORS

To determine the effective membrane thickness (EMT) experimentally, pure CO_2 permeation studies under conventional mode of operation with water as liquid membrane have been carried out. The governing equations for pure gas permeation (described in Section 2) were solved for different values of effective membrane thickness. The correct value should match the permeation rate of CO_2 obtained experimentally. The pure component permeation data for permeators #3, #6 and #8 are compared with the numerical results in Tables 4-8, 4-9 and 4-10, and the

Table 4-7

OBSERVED AND PREDICTED CO₂-N₂ SEPARATION FACTOR IN 20 WT%
DEA SOLUTION AT VARIOUS PARTIAL PRESSURES OF CO₂

Total Pressure cm Hg	P _u cm Hg	P _d cm Hg	ΔP_{CO_2} cm Hg	F _{Am} ¹	$\frac{1}{Q_{CO_2}}$ g ¹ /10	X	F _{Am} ²	$\frac{2}{Q_{CO_2}}$ g ² /10	X	α_{Am}^1	α_{Am}^2	α_{exp}
282.86	12.73	1.08	11.65	4.40	835.9		6.63	721.8		331.7	286.4	276.2
360.43	16.22	1.07	15.15	3.57	708.3		5.43	608.0		281.1	241.3	217.4
438.0	19.71	1.07	18.64	3.07	630.5		4.70	538.9		250.2	213.9	179.9
515.57	23.20	1.07	22.13	2.64	502.9		4.05	477.8		223.4	189.8	153.4
231.14	57.79	2.64	55.15	0.95	302.3		1.53	239.2		119.9	94.9	87.9
282.86	70.71	2.79	67.92	0.77	274.2		1.25	212.6		108.8	84.4	79.1
360.43	90.11	2.25	87.86	0.62	250.4		1.01	189.8		99.4	75.3	75.6
438.00	109.50	2.27	107.23	0.50	232.7		0.83	172.8		92.3	68.6	63.9
515.57	128.89	2.36	126.53	0.41	218.7		0.68	159.1		86.8	63.2	55.8

1 Diffusivity value calculated from Eq. (4-2)

2 Diffusivity value calculated from Eq. (4-3)

FIGURE 4-1
OBSERVED AND PREDICTED SEPARATION FACTOR
OF $CO_2 - N_2$ THROUGH AQUEOUS 20 WT% DEA SOLUTION

Table 4-8

PURE COMPONENT PERMEATION SIMULATION WITH VARIOUS VALUES OF MEMBRANE THICKNESS
AND COMPARISON WITH EXPERIMENTAL DATA IN PERMEATOR #3

Membrane Thickness inch X 10 ³	Feed Side Flow Rate scc/min inlet/outlet	Permeate Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Permeate Side Pressure psig inlet/outlet
4.39	125.0/5.96 150.0/22.28 175.0/44.31 200.0/58.96	0.0/119.04 0.0/127.72 0.0/130.69 0.0/141.04	15.3/12.76 16.5/13.20 17.20/13.0 18.5/13.67	5.56/2.0 5.76/2.0 5.79/2.0 6.04/2.0
4.5	125.0/8.54 150.0/25.05 175.0/47.17 200.0/62.04	0.0/116.46 0.0/124.95 0.0/127.83 0.0/137.96	15.3/12.69 16.5/13.14 17.2/12.92 18.5/13.60	5.49/2.0 5.69/2.0 5.71/2.0 5.97/2.0
4.75	125.0/14.01 150.0/30.93 175.0/53.20 200.0/68.55	0.0/110.99 0.0/119.07 0.0/121.80 0.0/131.45	15.3/12.55 16.5/13.0 17.2/12.77 18.5/13.43	5.34/2.0 5.53/2.0 5.56/2.0 5.80/2.0
5.0	125.0/18.98 150.0/36.27 175.0/58.68 200.0/74.47	0.0/106.02 0.0/113.73 0.0/116.32 0.0/125.53	15.3/12.43 16.5/12.85 17.2/12.63 18.5/13.28	5.20/2.0 5.39/2.0 5.41/2.0 5.64/2.0
Data	125.0/15.76 150.0/29.61 175.0/55.75 200.0/73.82	0.0/110.35 0.0/120.50 0.0/119.13 0.0/125.72	15.3/11.4 16.5/11.3 17.2/10.2 18.5/10.5	7.2/2.0 7.3/2.0 7.2/2.0 7.4/2.0

Feed: 99.99% CO₂; Shell Press.: 20 psig; Bath Temp.: 25°C; Membrane Liquid: Water

$Q_{CO_2} = 210.0 \times 10^{-9} \text{ (scc-cm/cm}^2 \text{ -s-cm Hg)}$

Table 4-9

PURE COMPONENT PERMEATION SIMULATION WITH VARIOUS VALUES OF MEMBRANE THICKNESS
AND COMPARISON WITH EXPERIMENTAL DATA IN PERMEATOR #6

Membrane Thickness inch X 10 ³	Feed Side Flow Rate scc/min inlet/outlet	Permeate Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Permeate Side Pressure psig inlet/outlet
4.39	100.0/35.39 125.0/61.42 150.0/84.83 200.0/139.05 150.0/91.69	0.0/64.54 0.0/63.51 0.0/65.10 0.0/60.89 0.0/58.25	15.5/14.41 15.5/14.00 16.0/14.12 15.6/12.81 14.7/12.68	2.05/2.0 2.05/2.0 2.05/2.0 2.05/2.0 2.05/2.0
4.5	100.0/36.98 125.0/63.00 150.0/86.44 200.0/140.55 150.0/93.13	0.0/62.95 0.0/61.94 0.0/63.49 0.0/59.38 0.0/56.81	15.5/14.40 15.5/13.98 16.0/14.11 15.6/12.80 14.7/12.66	2.05/2.0 2.05/2.0 2.05/2.0 2.05/2.0 2.05/2.0
4.75	100.0/40.33 125.0/66.29 150.0/89.82 200.0/143.72 150.0/96.16	0.0/59.60 0.0/58.65 0.0/60.11 0.0/56.22 0.0/53.78	15.5/14.37 15.5/13.95 16.0/14.08 15.6/12.77 14.7/12.64	2.05/2.0 2.05/2.0 2.05/2.0 2.05/2.0 2.04/2.0
Data	100.0/36.45 125.0/65.36 150.0/83.05 200.0/138.32 150.0/94.20	0.0/60.94 0.0/59.84 0.0/67.53 0.0/60.39 0.0/55.45	15.5/13.2 15.5/11.7 16.0/13.7 15.6/11.0 14.7/10.7	2.6/2.0 2.8/2.0 2.6/2.0 2.8/2.0 2.6/2.0

Feed: 99.99% CO₂; Shell Press.: 20 psig; Bath Temp.: 25°C; Membrane Liquid: Water

Q_{CO₂} = 210.0 x 10⁻⁹ (scc-cm/cm²-s-cm Hg)

Table 4-10

PURE COMPONENT PERMEATION SIMULATION WITH VARIOUS VALUES OF MEMBRANE THICKNESS
AND COMPARISON WITH EXPERIMENTAL DATA IN PERMEATOR #8

Membrane Thickness inch X 10 ³	Feed Side Flow Rate scc/min inlet/outlet	Permeate Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Permeate Side Pressure psig inlet/outlet
4.39	125.0/81.94 150.0/107.45 200.0/158.49	0.0/43.06 0.0/42.55 0.0/41.51	15.0/13.80 15.0/13.50 15.0/12.89	2.42/2.0 2.42/2.0 2.40/2.0
4.5	125.0/82.98 150.0/108.48 200.0/159.49	0.0/42.02 0.041.52 0.0/40.51	15.0/13.79 15.0/13.49 15.0/12.33	2.41/2.0 2.40/2.0 2.39/2.0
4.85	125.0/85.97 150.0/111.43 200.0/162.37	0.0/39.03 0.0/38.57 0.0/37.63	15.0/13.78 15.0/13.47 15.0/12.86	2.38/2.0 2.38/2.0 2.36/2.0
5.0	125.0/87.12 150.0/112.57 200.0/163.48	0.0/37.88 0.0/37.43 0.0/36.52	15.0/13.77 15.0/13.47 15.0/12.85	2.37/2.0 2.37/2.0 2.35/2.0
Data	125.0/85.36 150.0/112.4 200.0/161.8	0.0/39.25 0.0/37.88 0.0/36.83	15.0/13.6 15.0/13.3 15.0/13.0	5.8/2.0 5.7/2.0 5.5/2.0

Feed: 99.99% CO₂; Shell Press.: 20 psig; Bath Temp.: 25°C; Membrane Liquid: Water

$$Q_{\text{CO}_2} = 210.0 \times 10^{-9} \text{ (scc-cm/cm}^2\text{-s-cm Hg)}$$

effective membrane thicknesses are estimated to be 0.00475 inch, 0.0045 inch and 0.00485 inch, respectively.

The EMT can also be determined from actual separation run through water in the sweep gas mode by solving the three-component permeation model for several assumed values of d . The correct value should give a good agreement between calculated values and observed data. Table 4-11 shows the separation data and simulation results for Permeator #5. An EMT value of 0.00439 inch matched the data very well. As will be shown later, except for permeator #6, the EMT values for different permeators, thus determined, were in close agreement with the values determined from pure component permeation runs.

Table 4-12 shows that, for permeator #6, a value of $d=0.01$ inch gives a better agreement between observed data and calculated values. The discrepancy from the value obtained by pure component permeation run for permeator #6 is most likely due to the leakage from the defective fiber as well as condensation of water in the pores of the microporous fiber wall. This increased the resistance for mass transfer which is reflected in the higher membrane thickness. Moreover the separation runs were carried out at higher feed gas inlet pressure which required higher shell liquid pressure (note that, in a HFCLM permeator, the shell pressure is always maintained at a higher value than the gas streams pressures). Since the pressure drop in the sweep side was not that much, the larger diameter fibers were exposed to the high pressure differentials; that caused deformation of the larger diameter fibers. This deformation has not been incorporated in the three-component permeation model. When pressurized externally, single hollow fiber undergoes two types of deformation: radial and axial (Stern et al., 1977; Thorman and Hwang, 1978). As a result, the fiber cross section decreases and the length of the fiber increases. Both of these should cause an increase in the pressure drop in the larger bore fibers (discussed in separation studies section later). Apart from these, as the diameter decreases, the permeation rate due to reduction in cross sectional area decreases, which in turn increases the effective membrane thickness. The effect was not prominent in the case of smaller diameter fibers which are considered to be 'thick cylinders' (wall thickness: 25 micron, ID : 100 micron). Thus 0.01 inch membrane thickness was used in all numerical simulations of the performance of permeator #6. The effective membrane

Table 4-11

TERNARY PERMEATION MODEL SIMULATION WITH VARIOUS VALUES OF MEMBRANE THICKNESS
AND COMPARISON WITH EXPERIMENTAL DATA OF PERMEATOR #5

Membrane Thick- ness inchX10 ³	Feed Side Flow Rate scc/min Inlet/Outlet	Sweep Side Flow Rate scc/min Inlet/Outlet	Feed Side Pressure psig Inlet/Outlet	Sweep Side Pressure psig Inlet/Outlet	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *
2.0	100.0/42.34	200.0/257.66	45.0/43.6	16.7/2.0	61.34/0.00	13.21/15.53
4.39	100.0/53.99	200.0/246.02	45.0/43.5	16.5/2.0	79.78/0.00	6.88/16.26
7.0	100.0/57.02	200.0/242.98	45.0/43.4	16.5/2.0	86.55/0.09	4.38/16.44
Data	100.0/58.46	200.0/247.54	45.0/42.5	18.0/2.0	81.90/0.00	6.52/16.51

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Membrane Liquid: Water

Table 4-12

TERNARY PERMEATION MODEL SIMULATION WITH VARIOUS VALUES OF MEMBRANE THICKNESS
AND COMPARISON WITH EXPERIMENTAL DATA OF PERMEATOR #6

Membrane Thick- ness inchX10 ³	Feed Side Flow Rate scc/min Inlet/Outlet	Sweep Side Flow Rate scc/min Inlet/Outlet	Feed Side Pressure psig Inlet/Outlet	Sweep Side Pressure psig Inlet/Outlet	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *
4.5	150.0/92.63 150.0/92.28	200.0/257.37 300.0/357.72	45.0/43.95 45.0/43.95	1.03/0.5 1.27/0.5	90.73/6.05 91.03/5.60	2.32/21.12 1.68/15.31
6.0	150.0/98.97 150.0/98.5	200.0/251.03 300.0/351.50	45.0/43.9 45.0/43.9	1.03/0.5 1.27/0.5	86.62/11.07 87.01/10.58	1.7/19.52 1.22/14.09
7.5	150.0/104.58 150.0/104.09	200.0/245.42 300.0/345.91	45.0/43.86 45.0/43.87	1.03/0.5 1.27/0.5	82.90/15.33 83.27/14.88	1.35/17.9 0.96/12.86
10.0	150.0/112.03 150.0/111.61	200.0/237.97 300.0/338.39	45.0/43.83 45.0/43.83	1.02/0.5 1.26/0.5	78.20/20.53 78.49/20.19	1.0/15.53 0.71/11.06
Data	150.0/111.47 150.0/111.0	200.0/239.81 300.0/342.98	45.0/42.8 45.0/42.8	3.2/0.5 3.5/0.5	77.92/22.45 78.25/22.15	1.58/14.47 1.27/10.37

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Membrane Liquid: Water

thickness values of different permeators are reported in Table 4-13.

The EMT may be determined theoretically by solving the two-dimensional diffusion equation for a chemically non-reactive gas membrane system (Majumdar et al., 1989; NYSERDA Report 87-10). The analysis was based on the assumption that hollow fibers are arranged in square pitch. Thus for permeators #3, #4, #5 and #8, having the same packing density and fiber OD, a single EMT value of 0.00439 inch was calculated (Majumdar et al., 1989; NYSERDA Report 87-10). This theoretical prediction is in close agreement with the value obtained from pure component permeation run and from separation run.

Utilizing the generalized two-dimensional model, the effect of hollow fiber outside diameter and packing density on average effective liquid membrane thickness were calculated. The computed results, plotted in Figure 4-2, suggest that, the membrane thickness decreases almost linearly with decrease in fiber OD for a particular value of packing density. The same result was obtained by increasing the packing density while the fiber OD was kept constant. Therefore, it is possible to reduce the EMT value for HFCLM permeators provided hollow fibers of smaller OD are available.

PURIFICATION STUDIES OF MODEL BIOGAS MIXTURES IN SWEEP GAS MODE THROUGH DIFFERENT LIQUID MEMBRANES IN SMALL-SCALE OPERATION

Model biogas purification studies were carried out with different liquid membranes such as pure water, aqueous K_2CO_3 solution and aqueous solution of DEA. For pure water as membrane, the gas streams were not humidified. However, the streams were humidified completely when aqueous solution of either K_2CO_3 or DEA was used as membrane. All experiments were carried out at 25°C. Pure helium gas was normally used to pressurize the shell liquid storage tank.

The material balances were checked from the tables shown later and found to be within the error limit ($\pm 5\%$) of the electronic mass flowmeter readings. Thus the material balances were considered to be satisfactory. In all the figures, feed and sweep outlet mole fractions of CO_2 and N_2 or CH_4 are designated by CO_2/F , N_2/F or CH_4/F and CO_2/S , N_2/S or CH_4/S , respectively.

Table 4-13

EFFECTIVE MEMBRANE THICKNESS*
FOR DIFFERENT SMALL PERMEATORS

PERMEATOR NO.	THICKNESS MIL
3	4.39
5	4.39
6	10.00
8	4.85

* Determined from experimental separation data

FIGURE 4-2
EFFECTS OF HOLLOW FIBER SIZE AND PACKING DENSITY
ON LIQUID MEMBRANE THICKNESS

Water as Liquid Membrane and 40% CO₂ - 60% N₂ as Feed Gas

Steady state separation data for a model biogas feed mixture separation through pure water membrane in permeator #5 was already reported in Table 4-11. The nitrogen recovery (defined as the percentage of the fractional volume of nitrogen retained in the purified feed gas) was 79.8%. The data were used to determine the effective membrane thickness in the permeator. This value of membrane thickness was also obtained for permeator #3 (Majumdar, 1986; NYSERDA Report 87-10). We had carried out extensive separation studies in this mode using permeator #3 with water as liquid membrane. Thus it is expected that permeator #5 would give similar behavior as long as water is being used as liquid membrane.

Separation studies of the model biogas mixture in this mode with permeator #6 containing mixed fibers were carried out at two different pressures with pure water as membrane. To reduce the sweep stream pressure drop, the larger diameter fibers were used as sweep channel. The steady state data for a high feed inlet pressure (45 psig) are presented in Table 4-14. Both feed and sweep flow rate variations are shown. For feed flow variation studies, feed flow rates of 50 to 150 sccm were maintained. Pressure drop in the sweep side at the highest sweep gas flow rate of 400 sccm was only around 4 psi. It was possible to bring down the CO₂ concentration level to around 10% at the lowest feed flow rate. Note that, the effective length of the permeator is only 2 feet, i. e., it has only 40% of the membrane area of permeator #5. Due to the much lower sweep side pressure drop, helium permeation rate to the feed stream was quite low in this case when compared with that in permeator #5 as well as the earlier studies in permeators containing smaller diameter fibers (Majumdar et al., 1988). Nitrogen recovery was more than 90% in all the cases.

The data and the simulation results for feed gas flow variation studies are shown in Figure 4-3; those for sweep flow variation studies are shown in Figures 4-4 and 4-5 for two different feed flow rates where a membrane thickness of 0.01 inch was used for simulation. The simulation explains the data trends quite well. As expected, the CO₂ percentage in the purified gas increased with an increase in feed flow rate.

Table 4-14

PURIFICATION RUNS UNDER SWEEP GAS MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #6

Feed Side Flow Rate scc/min in/out	Sweep Side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep Side Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *	Nitrogen Recovery Percent- age
(A) Feed Flow Variation Studies						
50.0/30.39	200.0/220.36	45.0/44.3	3.7/0.5	90.36/9.23	1.91/7.61	91.5
100.0/69.47	200.0/232.13	45.0/43.5	3.6/0.5	80.70/19.38	2.02/11.42	93.4
150.0/111.47	200.0/239.81	45.0/42.8	3.2/0.5	77.92/22.45	1.58/14.47	95.6
100.0/68.65	300.0/332.91	45.0/43.5	3.8/0.5	83.59/15.89	1.19/8.73	95.6
150.0/111.0	300.0/342.98	45.0/42.8	3.5/0.5	78.25/22.15	1.27/10.37	96.5
(B) Sweep Flow Variation Studies						
100.0/69.47	200.0/232.13	45.0/43.5	3.6/0.5	80.7/19.38	2.02/11.42	93.4
100.0/68.65	300.0/332.91	45.0/43.5	3.8/0.5	83.59/15.89	1.19/8.73	95.6
100.0/68.87	400.0/433.43	45.0/43.5	4.5/0.5	83.90/16.04	0.96/6.61	96.3

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Membrane Liquid: Water

FIGURE 4-3
 FEED FLOW VARIATION STUDIES:
 SWEEP GAS MODE OF OPERATION IN PERMEATOR #6

FIGURE 4-4
 SWEEP FLOW VARIATION STUDIES:
 SWEEP GAS MODE OF OPERATION IN PERMEATOR #6

FIGURE 4-5
 SWEEP FLOW VARIATION STUDIES:
 SWEEP GAS MODE OF OPERATION IN PERMEATOR #6

Since the pure component permeation run was carried out at low pressure (~15 psig) the separation run was also carried out at low pressure to study the effect of shell pressure. Steady state results for feed flow variation studies at a low pressure (~16 psig) are presented in Table 4-15. The data and the simulation results for feed gas flow variation studies are compared in Figure 4-6 where again a membrane thickness of 0.01 inch was used for simulation. These results suggest that leakage of liquid as well as fiber deformation were still there. Note that, compared to the long permeator, the permeate fibers in permeator #6 were always exposed to higher membrane liquid pressure differential because of lower pressure drop. Comparing Tables 4-14 and 4-15 we see that the helium content in purified feed gas increased as the feed gas pressure was lowered. Higher sweep stream pressure drop in Table 4-14 suggests more leakage and deformation at higher shell liquid pressure.

The results of feed and sweep flow variation studies in permeator #8 are shown in Table 4-16. The CO₂ percentage in the purified gas stream varied from 6 - 12%, depending on the feed and sweep gas flow rates. The N₂ recovery in each run is also shown in the table. Generally, the N₂ recovery increased with an increase in the feed flow rate. The data and the simulation results for feed flow variation studies are shown in Figure 4-7, whereas those for sweep flow variation studies are shown in Figures 4-8 and 4-9. Effective membrane thickness used for simulation is 0.00485 inch. Better performance in permeator #8 compared to permeator #6 in terms of product quality was mainly due to the lower membrane thickness.

Water as Liquid Membrane and 40% CO₂ - 60% CH₄ as Feed Gas

Separation studies with CO₂-N₂ feed mixture and He sweep gas in permeator #6 (Table 4-14) showed that the helium content in purified feed gas was drastically reduced when the feed pressure was 45 psig. This implies that air can be used as sweep gas in the actual separation of a CH₄ - CO₂ mixture. It is clear that nitrogen and oxygen concentration in the purified biogas mixture would be very low. With that objective, a 90-hour purification run with a 40% CO₂ - 60% CH₄ feed was carried out with water as membrane in permeator #6 and permeator #7 connected in series. Pure nitrogen gas was used as a sweep. Both gas streams entering the permeator were completely dry. The flow rates of feed

Table 4-15

PURIFICATION RUNS UNDER SWEEP GAS MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #6

Feed Side Flow Rate scc/min in/out	Sweep Side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep Side Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *	Nitrogen Recovery Percentage
50.0/33.67	200.0/215.17	15.5/13.7	2.3/0.6	75.31/19.05	3.0/6.5	78.6
75.0/57.54	200.0/217.33	15.5/12.7	2.2/0.5	71.56/24.21	2.8/7.6	86.5
100.0/78.67	200.0/222.29	16.75/13.2	2.2/0.5	69.30/26.83	3.6/8.83	86.6

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 20 psig; Membrane Liquid: Water

FIGURE 4-6
FEED FLOW VARIATION STUDIES:
SWEEP GAS MODE OF OPERATION IN PERMEATOR #6

Table 4-16

PURIFICATION RUNS UNDER SWEEP GAS MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #8

Feed Side Flow Rate scc/min in/out	Sweep Side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep Side Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *	Nitrogen Recovery Percent- age
(A) Feed Flow Variation Studies						
50.0/23.4	175.0/202.6	45.0/44.25	8.0/2.0	86.05/6.08	5.20/9.50	67.13
75.0/38.7	175.0/214.6	45.0/44.0	8.3/2.0	85.59/9.02	5.68/13.00	73.61
100.0/56.7	175.0/223.7	45.0/44.0	9.0/2.0	83.96/12.29	5.81/15.62	79.4
(B) Sweep Flow Variation Studies						
50.0/29.3	200.0/218.6	45.4/44.5	11.6/2.0	84.50/9.12	2.32/7.87	82.41
50.0/23.4	175.0/202.6	45.0/44.25	8.0/2.0	86.05/6.08	5.20/9.50	67.13
50.0/26.64	100.0/124.3	45.0/44.0	5.6/2.0	87.5/7.13	5.89/15.34	77.69
75.0/38.7	175.0/214.6	45.0/44.0	8.3/2.0	85.59/9.02	5.68/13.00	73.61
75.0/41.4	134.0/171.0	45.0/44.0	6.8/2.0	85.66/9.96	6.07/16.17	78.81
75.0/41.5	94.0/129.8	45.0/44.0	5.5/2.0	85.63/10.49	8.14/21.14	79.0

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Membrane Liquid: Water

FIGURE 4-7
 FEED FLOW VARIATION STUDIES:
 SWEEP GAS MODE OF OPERATION IN PERMEATOR #8

FIGURE 4-8
 SWEEP FLOW VARIATION STUDIES:
 SWEEP GAS MODE OF OPERATION IN PERMEATOR #8

FIGURE 4-9
 SWEEP FLOW VARIATION STUDIES:
 SWEEP GAS MODE OF OPERATION IN PERMEATOR #8

and sweep gas streams were 50 sccm and 350 sccm, respectively. The shell side water membrane was pressurized by a helium gas cylinder. The results of this experiment are presented in Table 4-17. Steady performance was achieved with an average CH_4 recovery of 87% in the purified biogas. Note that the purified gas stream contained only 5.5% CO_2 . The permeation rate of sweep N_2 into the feed gas was very low due to the much lower pressure drop in the large bore sweep fibers. The N_2 content in the purified gas stream was only 2.5%. Figure 4-10 graphically shows the membrane stability in this long-term run.

These results demonstrate that air can be used as sweep gas in actual operation. If air (80% N_2 - 20% O_2) were used instead of N_2 as sweep gas, the O_2 composition in the purified gas stream would have been close to 0.5%. Further this run shows that the pressure drop in the sweep gas is only around 5 psi. This has to be compared with the 17 - 30 psi pressure drop encountered earlier with permeators containing smaller diameter fibers (NYSERDA Report 87-10). It is possible to make additional changes in such a mode of operation with separate sweep gas streams entering each permeator. This will reduce the sweep pressure drop to half the level observed here. That will reduce the N_2 permeation rate and N_2 content of the purified biogas still further. In fact, such a mode of operation may even be feasible with the smaller diameter fibers.

Table 4-18 provides the steady state data taken with feed and sweep flow rates maintained at 50 sccm and 200 sccm, respectively using permeator #8. Nitrogen gas was used as sweep. Simulation results based on the permeability of CO_2 , CH_4 and N_2 through water are also presented in the same table. The simulation describes the data satisfactorily. Note that, the result can be compared with the corresponding run for CO_2 - N_2 feed gas mixture and helium sweep gas (4th row, Table 4-16), provided the permeability of the gases are taken into consideration. As expected, recovery of N_2 is more compared to CH_4 as the latter is more permeable through water. On the other hand sweep helium being more permeable than sweep N_2 results in a higher composition of CH_4 compared to that of N_2 in the purified gas.

30 wt% K_2CO_3 Solution as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas

Separation runs of model biogas mixture (40% CO_2 - 60% N_2) with 30% K_2CO_3

Table 4-17

MODEL BIOGAS PURIFICATION STUDIES WITH WATER AS LIQUID MEMBRANE
IN PERMEATOR #6 AND #7 CONNECTED IN SERIES

Elas- Time hrs.	Feed Side Flow Rate scc/min Inlet/Outlet	Sweep Side Flow Rate scc/min Inlet/Outlet	Feed Side Pressure psig Inlet/Outlet	Sweep Side Pressure psig Inlet/Outlet	Feed Outlet Composition Percentage CH ₄ /CO ₂ *	Sweep Outlet Composition Percentage CH ₄ /CO ₂ *
2.5	50.0/28.23	350.0/370.56	45.0/43.8	6.0/2.0	81.78/12.45	1.56/5.09
6	50.0/27.80	350.0/371.96	45.3/43.8	6.5/2.0	90.66/5.60	1.56/5.07
10	50.0/27.80	350.0/371.87	45.2/43.8	7.5/2.6	90.95/5.58	1.51/5.00
14	50.0/27.74	350.0/371.36	45.2/43.8	6.6/1.5	91.17/5.86	1.48/4.92
18	50.0/27.73	350.0/371.46	45.3/43.8	6.3/1.5	91.84/5.50	1.48/4.98
22	50.0/27.74	350.0/371.73	45.3/43.8	6.4/1.5	91.85/5.44	1.46/5.02
26	50.0/27.74	350.0/371.88	45.4/43.8	6.5/1.6	92.05/5.24	1.46/5.07
30	50.0/28.56	350.0/372.13	45.4/43.8	6.5/1.6	92.16/5.04	1.42/5.11
33	50.0/28.14	350.0/371.86	45.4/43.8	6.7/1.6	91.94/5.37	1.42/5.09
37	50.0/28.14	350.0/371.46	45.5/43.8	6.6/1.65	92.83/4.62	1.43/5.09
41	50.0/28.14	350.0/371.69	45.5/43.8	6.4/1.1	92.64/4.87	1.36/5.05
45	50.0/28.10	350.0/371.62	45.5/43.8	6.5/1.6	92.93/5.02	1.42/5.08
49	50.0/28.51	350.0/371.62	45.6/43.8	6.5/1.6	92.39/5.45	1.46/5.10

Table 4-17 (contd.)

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage CH ₄ /CO ₂ *	Composition Percentage CH ₄ /CO ₂ *	Composition Percentage CH ₄ /CO ₂ *	Composition Percentage CH ₄ /CO ₂ *
54	50.0/28.11		350.0/371.53		45.6/43.8		6.4/1.6		92.36/5.40		1.42/5.11	
58	50.0/28.12		350.0/372.04		45.6/43.8		7.2/2.2		92.26/5.35		1.40/5.09	
61	50.0/28.10		350.0/371.76		45.7/43.8		6.5/1.8		92.65/5.29		1.38/5.12	
65	50.0/28.51		350.0/371.82		45.7/43.8		6.5/1.8		92.89/5.03		1.34/5.07	
69	50.0/28.10		350.0/371.26		45.8/43.8		6.4/1.6		93.01/5.06		1.38/5.14	
74	50.0/28.12		350.0/371.82		45.8/43.7		6.4/1.6		92.79/4.95		1.43/5.11	
78	50.0/28.10		350.0/371.28		46.3/43.8		6.5/1.6		92.36/5.51		1.41/5.07	
82	50.0/28.08		350.0/371.46		46.2/43.8		6.3/1.6		92.40/5.75		1.41/4.94	
84	50.0/28.08		350.0/371.73		46.5/43.8		6.3/1.65		92.12/6.00		1.40/5.06	
86	50.0/28.09		350.0/371.76		46.5/43.8		6.5/1.7		92.25/5.77		1.40/5.00	
90	50.0/28.09		350.0/371.58		46.5/43.8		6.5/1.7		92.08/5.85		1.40/5.01	

* Balance Nitrogen; Feed: 40%CO₂-60%CH₄; Bath Temp.: 25°C; Sweep: Nitrogen;
Shell Press.: 50 psig; Average CH₄ Recovery: 87%

FIGURE 4-10
CLM STABILITY STUDIES: SWEEP GAS MODE
OF OPERATION WITH WATER AS MEMBRANE USING
PERMEATORS #6 AND #7 CONNECTED IN SERIES

Table 4-18

EXPERIMENTAL DATA AND SIMULATION RESULTS OF PURIFICATION RUN UNDER SWEEP GAS
MODE OF OPERATION WITH MODEL BIOGAS AND WATER AS MEMBRANE IN PERMEATOR #8

Feed Side Flow Rate scc/min in/out	Sweep Side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep Side Pressure psig in/out	Feed Outlet Composition Percentage CH ₄ /CO ₂ *	Sweep Outlet Composition Percentage CH ₄ /CO ₂ *	Methane Recovery Percent- age
Data						
50.0/23.8	200.0/224.96	45.0/44.5	12.0/2.0	87.88/8.95	4.0/7.92	69.72
Simulation ⁺						
50.0/23.05	200.0/226.95	45.0/44.86	6.4/2.0	93.63/0.17	3.71/8.80	71.93

* Balance Nitrogen; Feed: 40%CO₂-60%CH₄; Bath Temp.: 25°C; Sweep: Nitrogen;

Shell Press.: 50 psig; Membrane Liquid: Water
+ Membrane thickness used: 0.00485 inch

solution as membrane were carried out in permeator #5. Table 4-19 shows steady state data from four different runs. Feed pressure was maintained at 30 psig for the first two runs; it is expected that, at the lower pressure, facilitation would be higher. The first data set indicated for 50 sccm feed was obtained by running the system for 24 hours. The compositions, flow rates and pressures remained steady and stable. The same run was continued for another 30 hours with the feed flow rate changed to 100 sccm. Performance was stable in all respects in both the cases; N_2 recoveries were also very high. However, the percentage of CO_2 in the feed outlet stream was not that low. This can be due to lower permeability of CO_2 in the 30% K_2CO_3 solution at 25°C and also possibly due to the lower feed pressure.

The previous run was then continued by increasing the feed inlet pressure to 45 psig. Feed and sweep gas flow rates were adjusted to 50 sccm and 350 sccm, respectively. The run was continued for 24 hours but the CO_2 removal efficiency did not change significantly. The same run was continued for another 30 hours by increasing the feed flow rate to 100 sccm. Surprisingly enough, the pressure remained steady but the performance deteriorated with respect to CO_2 composition in the feed outlet. The steady state data, shown in Table 4-19 suggest that the mass transfer resistance increased with the progress of the run. This may be attributed to condensation of water in the defective pores in the microporous wall of the fibers containing salt solution or some kind of deposition of fine salt particles which might have caused significant increase in the effective membrane thickness. In the traditional absorption process carried out below 40°C, the solution strength is limited to about 12 wt% K_2CO_3 to avoid precipitation (Astarita et al., 1983). The numerical simulation results and the steady state values are also compared in the same table. Simulation results based on simple diffusion with no reaction predicts the data quite well. Simulation results based on other approximations (Otto and Quinn, 1971) predict a higher permeation rate of CO_2 .

In order to check whether there is really any fouling of the pores of the microporous hollow fibers, permeator #5 was thoroughly cleaned after completion of the separation experiments with K_2CO_3 solution as the liquid membrane. The following cleaning procedure was adopted. Shell side was flushed with distilled water for a long period. Then shell side was filled with water and pressurized

Table 4-19

SIMULATION RESULTS AND STEADY STATE DATA UNDER SWEEP GAS MODE OF OPERATION
WITH MODEL BIOGAS AND 30 WT% K₂CO₃ SOLUTION AS MEMBRANE IN PERMEATOR #5

Feed Side Flow Rate scc/min in/out	Sweep Side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep Side Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *	Nitrogen Recovery Percentage
Data						
+50.0/36.67	100.0/112.73	30.0/28.3	9.4/2.0	84.11/11.51	1.18/14.41	95.6
+100.0/81.45	100.0/119.67	30.25/27.1	9.5/2.0	75.07/23.32	1.06/18.51	97.9
+50.0/39.7	350.0/356.44	45.0/44.0	24.2/2.0	76.36/16.22	0.48/3.70	94.3
+100.0/81.03	350.0/368.20	45.0/43.0	22.5/2.0	74.9/21.52	0.50/6.05	96.9
¹ Simulation						
50.0/34.56	100.0/115.44	30.5/29.21	10.42/2.0	82.29/13.01	1.17/13.43	95.49
100.0/81.15	100.0/118.85	30.25/27.40	10.53/2.0	72.44/25.80	1.02/16.04	97.98
50.0/32.20	350.0/367.81	45.0/44.08	23.64/2.0	87.27/6.53	0.52/4.87	97.16
100.0/75.36	350.0/374.64	45.0/42.96	23.80/2.0	77.35/19.94	0.46/6.67	97.16
² Simulation						
50.0/29.86	100.0/120.14	30.5/29.35	10.4/2.0	95.21/0.04	1.30/16.64	94.77
100.0/68.59	100.0/131.41	30.25/27.60	10.76/2.0	85.54/12.45	1.01/23.94	97.79
100.0/62.64	350.0/387.36	45.0/43.15	23.92/2.0	92.70/4.04	0.50/9.67	96.78

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Membrane Liquid: 30 wt% K₂CO₃ solution; 100% Humidified feed and sweep gas;
+₁Shell Pressure : 35 psig; +₂Shell Pressure : 50 psig; -₉ scc-cm/(cm²-s-cm Hg);
Q_{CO₂} = 24.0 X 10⁻⁹ scc-cm/(cm²-s-cm Hg); Q_{N₂} = 0.682 X 10⁻⁹ scc-cm/(cm²-s-cm Hg);
Q_{He} = 1.192 X 10⁻⁹ scc-cm/(cm²-s-cm Hg) were used for simulation.

² Simulation was based on Otto and Quinn (1971)

gradually upto 50 psig and water was passed through both the tube sides for 24 hrs. Finally the permeator was dried using N_2 gas. Separation experiments were then again carried out in permeator #5 with CO_2 - N_2 feed gas and He sweep gas having pure water as a liquid membrane. The results are presented in Table 4-20 and they are quite different from those obtained earlier (see data in Table 4-11). The results suggest that there is some kind of irreversible fouling of the pores in the microporous hollow fibers by the fine crystals of K_2CO_3 salt which enhances the condensation in the pores, and thereby increases the membrane thickness.

Aqueous Solution of DEA as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas

Purification runs for model biogas mixture were also carried out with aqueous 10, 20 and 30 wt% solutions of diethanolamine (DEA) as liquid membranes using permeator #8. The steady state data for both feed and sweep flow variation studies with 10 wt% DEA as membrane are shown in Table 4-21. Similarly the results for 20 and 30 wt% DEA are shown in Tables 4-22 and 4-23, respectively. In all these studies, a gas mixture containing 40% CO_2 - 60% N_2 was used as feed and pure helium was introduced as sweep. Both the feed and sweep gases were completely humidified. Feed gas inlet pressure was maintained at 45 psig in all experiments except one run with 30 wt% DEA where it was maintained at 25 psig.

As expected, the CO_2 percentage in the purified model biogas increased with an increase in feed gas flow rate for all experiments. However, for 10 wt% DEA as liquid membrane, an increase in the sweep flow rate for a certain feed flow rate of 100 sccm did not improve the level of feed gas purification (Table 4-21), suggesting saturation of the carrier in the membrane: the downstream partial pressure of CO_2 has very little effect.

Simulation results are also presented in respective tables. An average permeability of CO_2 was determined corresponding to each run; a particular value, that predicted the compositions of feed and sweep outlet as well as nitrogen recovery well, was chosen. Highest separation factor (Q_{CO_2}/Q_{N_2}) was obtained in the case of 30 wt% DEA; however, CO_2 composition at feed outlet was relatively high compared to the results obtained with 10 wt% and 20 wt% DEA

Table 4-20

PURIFICATION RUNS UNDER SWEEP GAS MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #5

Feed Side Flow Rate scc/min in/out	Sweep Side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep Side Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *	Nitrogen Recovery Percent- age
100.0/81.53	200.0/217.3	46.5/43.0	21.0/2.0	69.38/26.42	1.18/7.93	94.27
50.0/37.09	200.0/210.68	45.2/43.0	20.5/2.0	74.75/19.70	1.00/5.83	92.42

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;

Shell Press.: 50 psig; Membrane Liquid: Water

Table 4-21

SIMULATION RESULTS AND STEADY STATE DATA OF PURIFICATION RUN WITH MODEL BIOGAS
IN SWEEP GAS MODE AND 10 WT% DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

$Q_{CO_2}^+$ $\times 10^9$	Feed Side Flow Rate scc/min in/out	Sweep side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep side Pressure psig in/out	Feed Outlet Composition Percentage N_2/CO_2^*	Sweep outlet Nitrogen Recovery Percentage N_2/CO_2^*	Percentage tage
Simulation							
95	50/31.70	200/218.30	45.25/45.0	6.2/1.0	86.19/6.82	1.23/8.17	91.08
115	75/50.18	200/224.82	45.3/44.9	6.2/1.0	84.50/10.96	1.16/10.9	94.22
130	100/70.40	100/129.60	45.0/44.5	3.9/1.0	81.67/15.46	1.93/22.47	95.83
130	100/69.94	200/230.06	45.0/44.5	6.3/1.0	82.18/14.53	1.10/12.97	95.79
125	100/70.48	300/329.52	45.1/44.6	8.4/1.0	81.56/14.9	0.76/8.95	95.80
Data							
50/32.59	200/210.11	45.25/44.5	6.0/1.0	84.27/9.15	1.22/8.12	91.60	
75/50.83	200/219.34	45.3/44.5	6.0/1.0	83.21/12.07	1.20/10.91	94.07	
100/70.89	100/127.78	45.0/44.2	3.8/1.0	80.00/16.73	1.76/22.47	94.52	
100/70.03	200/225.96	45.0/44.2	6.0/1.0	81.45/14.53	1.10/12.97	95.07	
100/69.87	300/327.66	45.1/44.2	8.1/1.0	81.41/15.03	0.66/8.98	94.81	

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;

Shell Press.: 50 psig; 100% Humidified feed and sweep gas;

+ Permeability of CO₂ in scc-cm/cm² -s-cm Hg;

$$Q_{N_2} = 3.86 \times 10^{-9} \text{ scc-cm/cm}^2 \text{ -s-cm Hg; } Q_{He} = 9.045 \times 10^{-9} \text{ scc-cm/cm}^2 \text{ -s-cm Hg}$$

Table 4-22

SIMULATION RESULTS AND STEADY STATE DATA OF PURIFICATION RUN WITH MODEL BIOGAS
IN SWEEP GAS MODE AND 20 WT% DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

$Q_{CO_2}^+$ $\times 10^9$	Feed Side Flow Rate scc/min in/out	Sweep side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep side Pressure psig in/out	Feed Outlet Composition Percentage N_2/CO_2^*	Sweep outlet Composition Percentage N_2/CO_2^*	Nitrogen Recovery Percent- tage
Simulation							
115	50/31.90	100/118.10	45.0/44.80	4.7/2.0	88.46/4.63	1.51/15.69	94.06
115	50/31.97	200/218.03	45.0/44.8	6.9/2.0	88.23/4.17	0.82/8.56	94.03
115	75/51.52	200/223.48	45.0/44.6	7.0/2.0	84.08/11.06	0.75/10.88	96.26
Data							
	50/31.96	100/112.73	45.0/44.5	4.5/2.0	88.46/9.12	1.64/15.55	94.24
	50/32.66	200/208.27	45.0/44.5	6.7/2.0	90.11/6.29	1.15/7.82	95.00
	75/50.40	200/217.33	45.0/44.4	6.7/2.0	85.88/12.33	0.88/10.73	96.20

* Balance Helium; Feed: 40% CO_2 -60% N_2 ; Bath Temp.: 25°C; Sweep: Helium;

Shell Press.: 50 psig; 100% Humidified feed and sweep gas;

+ Permeability of CO_2 in scc-cm/cm² -s-cm Hg;

$Q_{N_2} = 2.5165 \times 10^{-9}$ scc-cm/cm² -s-cm Hg; $Q_{He} = 9.52 \times 10^{-9}$ scc-cm/cm² -s-cm Hg;

Table 4-23

SIMULATION RESULTS AND STEADY STATE DATA OF PURIFICATION RUN WITH MODEL BIOGAS
IN SWEEP GAS MODE AND 30 WT% DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

$Q_{CO_2}^+$ x 10^9	Feed Side		Sweep side		Feed Side		Sweep side		Feed Outlet		Sweep outlet	
	Flow Rate	Pressure	Flow Rate	Pressure	Flow Rate	Pressure	Flow Rate	Pressure	Composition	Percentage	Composition	Percentage
	scc/min	psig	scc/min	psig	scc/min	psig	scc/min	psig	N ₂ /CO ₂ *	N ₂ /CO ₂ *	N ₂ /CO ₂ *	N ₂ /CO ₂ *
	in/out	in/out	in/out	in/out	in/out	in/out	in/out	in/out				
Simulation												
60	50/36.65	45.1/44.8	200/213.35	6.1/1.0	79.06/15.23	0.48/6.76	96.59					
85	50/37.76	25.0/24.6	200/212.24	6.1/1.0	77.68/16.59	0.32/6.47	97.77					
70	100/81.33	45.0/44.4	200/218.67	6.2/1.0	72.58/24.74	0.44/9.09	98.39					
Data												
	50/36.56	45.1/44.5	200/206.0	6.0/1.0	77.70/18.31	0.25/6.80	94.68					
	50/37.58	25.0/24.3	200/206.1	5.9/1.0	76.92/17.18	0.24/5.95	96.35++					
	100/79.66	45.0/44.0	200/213.2	6.3/1.0	73.33/24.39	0.30/8.62	97.35					

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; 100% Humidified feed and sweep gas; ++Shell Press: 30 psig;
+ Permeability of CO₂ in scc-cm/cm² -s-cm Hg;

$$Q_{N_2} = 1.40 \times 10^{-9} \text{ scc-cm/cm}^2 \text{ -s-cm Hg; } Q_{He} = 8.355 \times 10^{-9} \text{ scc-cm/cm}^2 \text{ -s-cm Hg}$$

under identical conditions. Note that, with 30 wt% DEA as liquid membrane, the performance at low feed pressure was more or less similar to that obtained with the high pressure run (Table 4-23) even though the partial pressure driving force for CO_2 was much less in the first case. This is due to higher facilitation of CO_2 , normally achieved at lower partial pressure of CO_2 . As expected nitrogen recovery was also slightly higher.

The solution having a composition of 20 wt% DEA was found to be the best liquid membrane both from the point of purity of the feed gas as well as recovery of nitrogen. Figure 4-11 shows the DEA concentration variation studies at a particular feed and sweep gas flowrate. Quality of the purified gas as well as recovery of N_2 improved as the concentration of DEA increased up to 20 wt%. However, in spite of high recovery, the quality of the purified feed gas deteriorated drastically when the concentration of DEA was increased to 30 wt%. This is most likely due to a change in the reaction kinetics at the higher amine concentrations (Blauwhoff et al., 1983). Smith and Quinn (1979) observed similar phenomena for facilitated transport of CO_2 through MEA and DEA solutions. Much slower transport rates at higher concentration as well as an apparent decrease in the reaction rate as all species concentration increases were also observed by Donaldson and Nguyen (1980).

Long-term stability runs for 10, 20 and 30 wt% DEA solutions are shown in Tables 4-24, 4-25 and 4-26, respectively. Steady performance was obtained in all runs unless there was a change in the surrounding temperature. Variation in room temperature as well as bath temperature affected the performance which was expected as the reaction rates were temperature dependent. Figures 4-12, 4-13 and 4-14 show the plots of the above three stability runs.

To study the effect of temperature on model biogas separation, a long-term experiment was carried out at a higher temperature using aqueous 20 wt% DEA solution as the liquid membrane in permeator #8. Generally, the rate of a reaction increases with an increase in temperature. It was speculated that better purification would be achieved as more CO_2 would permeate from the feed to the sweep side due to an increase in the rate of reaction between CO_2 and DEA.

FIGURE 4-11
 DEA CONCENTRATION VARIATION STUDIES:
 SWEEP GAS MODE OF OPERATION IN PERMEATOR #8

Table 4-24

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP GAS MODE
AND 10 WT% DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Sweep Side Flow Rate scc/min		Feed Side Pressure psig		Sweep Side Pressure psig		Feed Outlet Composition Percentage N ₂ /CO ₂ *		Sweep Outlet Composition Percentage N ₂ /CO ₂ *	
	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	N ₂ /CO ₂ *	N ₂ /CO ₂ *	N ₂ /CO ₂ *	N ₂ /CO ₂ *
5	75.0/50.24	200.0/219.53	45.0/44.3	6.1/1.0	83.87/11.07	1.22/11.14						
7	75.0/50.66	200.0/219.63	45.0/44.3	6.2/1.0	83.58/11.48	1.23/11.04						
9	75.0/50.09	200.0/219.63	45.0/44.3	6.2/1.0	83.39/11.83	1.24/11.03						
24	75.0/50.93	200.0/219.28	45.0/44.3	6.1/1.0	83.20/12.43	1.20/10.94						
26	75.0/50.97	200.0/218.81	45.0/44.3	6.1/1.0	83.04/12.41	1.22/10.92						
28	75.0/50.49	200.0/208.82	45.0/44.3	6.1/1.0	83.04/12.34	1.22/10.91						
30	75.0/50.54	200.0/218.79	45.2/44.3	6.1/1.0	82.90/12.28	1.21/10.95						
32	75.0/51.01	200.0/218.75	45.2/44.3	6.1/1.0	82.97/12.32	1.21/10.99						
34	75.0/50.50	200.0/218.78	45.2/44.3	6.1/1.0	83.10/12.27	1.23/10.95						
77	75.0/51.6	200.0/220.4	45.4/44.5	5.9/1.0	83.26/11.83	1.15/10.36						
79	75.0/51.48	200.0/219.9	45.3/44.5	6.0/1.0	83.00/12.37	1.14/10.84						
95	75.0/51.50	200.0/219.81	45.3/44.5	6.0/1.0	83.13/12.24	1.14/10.92						

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Shell liquid pressurized with helium;
100% Humidified feed and sweep gas; Average N₂ Recovery: 94%

Table 4-25

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP GAS MODE
AND 20 WT% DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

Elapsed Time hrs.	Feed Side Flow Rate scc/min Inlet/Outlet	Sweep Side Flow Rate scc/min Inlet/Outlet	Feed Side Pressure psig Inlet/Outlet	Sweep Side Pressure psig Inlet/Outlet	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *
2	50.0/30.15	200.0/210.02	45.0/44.1	7.8/2.0	92.68/0.86	1.78/6.99
4	50.0/32.17	200.0/211.54	45.0/44.1	7.3/2.0	87.97/3.97	1.79/7.39
7	50.0/33.01	200.0/212.27	44.7/44.2	7.0/2.0	84.51/7.15	1.75/7.64
9	50.0/33.28	200.0/210.65	44.7/44.2	6.8/2.0	83.88/8.81	1.58/7.45
12.5	50.0/33.14	200.0/210.80	44.7/44.2	6.8/2.0	82.82/10.2	1.52/7.41
25	50.0/33.19	200.0/209.32	44.8/44.2	6.8/2.0	82.98/9.85	1.52/7.86
27	50.0/32.63	200.0/210.31	44.9/44.1	6.8/2.0	83.03/10.08	1.49/7.86
29	50.0/32.70	200.0/211.34	44.9/44.1	6.8/2.0	83.08/9.69	1.47/7.79
31	50.0/33.17	200.0/211.35	44.9/44.1	6.8/2.0	82.73/10.09	1.46/7.79
33	50.0/33.17	200.0/211.35	44.9/44.1	6.8/2.0	82.37/10.31	1.44/7.80
37.5	50.0/32.17	200.0/210.24	44.9/44.1	6.8/2.0	82.62/10.15	1.50/7.91
49	50.0/35.66	200.0/207.72	44.9/44.1	6.8/2.0	79.21/14.83	1.19/6.75 ⁺

Table 4-25 (contd.)

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Sweep Side Flow Rate scc/min		Feed Side Pressure psig		Sweep Side Pressure psig		Feed Outlet Composition Percentage N ₂ /CO ₂ *		Sweep Outlet Composition Percentage N ₂ /CO ₂ *	
	Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		N ₂ /CO ₂ *		N ₂ /CO ₂ *	
51	50.0/35.81		200.0/211.82		44.9/44.1		6.8/2.0		78.90/14.30		1.42/7.83	
54.5	50.0/33.12		200.0/210.64		44.9/44.2		6.8/2.0		82.23/10.70		1.36/7.60	
56	50.0/33.37		200.0/210.65		44.9/44.2		6.8/2.0		81.82/11.00		1.34/7.61	
58.5	50.0/33.34		200.0/211.41		44.9/44.2		6.8/2.0		81.59/11.30		1.38/7.78	
73	50.0/33.08		200.0/212.11		44.9/44.2		6.9/2.0		84.34/8.16		1.40/8.03 ⁺⁺	
74	50.0/32.84		200.0/212.18		44.9/44.2		6.9/2.0		81.44/8.15		1.37/7.89	
75	50.0/33.19		200.0/212.39		44.9/44.2		6.9/2.0		81.58/8.38		1.34/7.79	
77	50.0/33.13		200.0/212.42		44.9/44.2		6.9/2.0		81.64/8.42		1.33/7.76	
79	50.0/33.12		200.0/211.39		44.9/44.2		6.9/2.0		81.92/8.41		1.35/7.83	
81.5	50.0/33.08		200.0/208.89		44.9/44.2		6.8/2.0		81.77/8.43		1.21/8.50	
83.5	50.0/33.61		200.0/211.94		44.9/44.2		6.8/2.0		81.72/8.40		1.24/7.90	
97	50.0/33.33		200.0/212.24		44.9/44.2		6.8/2.0		81.54/8.32		1.31/7.86	

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;

Shell Press.: 50 psig; Shell liquid pressurized with helium; 100% Humidified feed and sweep gas;

⁺ Bath Temperature dropped to 15°C;

⁺⁺ Bath Temperature was maintained at 30°C for next 24 hrs.

Table 4-26

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP GAS MODE
AND 30 WT% DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *
2.5	100.0/77.20	200.0/213.93	200.0/213.93	45.0/44.0	7.1/1.0	81.82/15.15	0.51/8.69					
4.5	100.0/79.15	200.0/214.00	200.0/214.00	45.0/44.0	6.8/1.0	79.14/17.81	0.45/8.66					
7	100.0/78.80	200.0/213.87	200.0/213.87	45.0/44.0	6.7/1.0	77.61/19.46	0.42/8.81					
11	100.0/78.48	200.0/213.78	200.0/213.78	45.0/44.0	6.5/1.0	76.61/20.70	0.36/8.39					
12	100.0/78.37	200.0/213.74	200.0/213.74	45.0/44.0	6.5/1.0	76.33/21.10	0.36/8.98					
22	100.0/80.16	200.0/213.34	200.0/213.34	44.8/44.0	6.4/1.0	73.37/24.13	0.30/8.46					
24	100.0/79.21	200.0/213.90	200.0/213.90	44.8/44.0	6.4/1.0	73.40/24.11	0.31/8.86					
26.5	100.0/79.94	200.0/212.54	200.0/212.54	44.8/44.0	6.3/1.0	73.05/24.76	0.27/8.32					
28.5	100.0/79.24	200.0/213.14	200.0/213.14	44.8/44.0	6.3/1.0	73.15/24.57	0.28/8.67					
32.5	100.0/79.10	200.0/210.97	200.0/210.97	44.8/44.0	6.3/1.0	73.83/24.25	0.28/8.84					
47	100.0/84.11	200.0/206.60	200.0/206.60	44.8/44.0	6.0/1.0	68.92/29.26	0.19/6.58					
48	100.0/81.54	200.0/211.10	200.0/211.10	44.8/44.0	6.1/1.0	68.95/28.14	0.23/7.87					

Table 4-26 (contd.)

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Sweep Side Flow Rate scc/min		Feed Side Pressure psig		Sweep Side Pressure psig		Feed Outlet Composition Percentage N ₂ /CO ₂ *		Sweep Outlet Composition Percentage N ₂ /CO ₂ *	
	Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		N ₂ /CO ₂ *		N ₂ /CO ₂ *	
53	100.0/78.47		200.0/213.68		44.8/44.0		6.2/1.0		72.95/24.90		0.26/8.92	
54	50.0/37.20		200.0/207.46		45.0/44.5		6.1/1.0		73.00/24.76		0.29/7.66 ⁺	
70.5	50.0/38.05		200.0/204.51		45.1/44.5		6.0/1.0		76.59/20.88		0.24/5.70	
75.5	50.0/36.36		200.0/205.90		45.1/44.5		6.0/1.0		78.53/18.63		0.26/6.28	
79.5	50.0/36.38		200.0/205.83		45.0/44.5		6.0/1.0		78.87/18.32		0.26/6.31	
93	50.0/35.85		200.0/205.88		45.1/44.5		6.0/1.0		79.14/18.38		0.24/6.31	
94	50.0/36.77		200.0/206.09		45.1/44.5		6.0/1.0		76.91/17.86		0.26/6.08	
95	50.0/36.76		200.0/206.13		45.1/44.5		6.0/1.0		76.39/18.22		0.24/6.05	
96	50.0/37.21		200.0/206.16		45.1/44.5		6.0/1.0		76.35/18.43		0.23/6.02	
97	50.0/37.70		200.0/206.43		45.1/44.5		6.0/1.0		75.49/18.80		0.21/5.75	
100	50.0/37.53		200.0/206.45		45.1/44.5		6.0/1.0		74.75/20.18		0.22/5.72	

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Shell liquid pressurized with helium; 100% Humidified feed and
sweep gas;

⁺ Feed side flow rate was changed to 50 scc/min

FIGURE 4-12
 CLM STABILITY STUDIES: SWEEP GAS MODE OF OPERATION
 WITH AQUEOUS 10 WT% DEA SOLUTION AS MEMBRANE
 IN PERMEATOR #8

FIGURE 4-13
CLM STABILITY STUDIES: SWEEP GAS MODE OF OPERATION
WITH AQUEOUS 20 WT% DEA SOLUTION AS MEMBRANE
IN PERMEATOR #8

FIGURE 4-14
 CLM STABILITY STUDIES: SWEEP GAS MODE OF OPERATION
 WITH AQUEOUS 30 WT% DEA SOLUTION AS MEMBRANE
 IN PERMEATOR #8

In order to carry out the separation study at an elevated temperature, a few modifications of the small-scale purification loop were made. Two membrane humidifiers were added to the existing feed and sweep gas humidifier vessels. These membrane humidifiers were kept in a separate constant temperature bath. The temperature of this bath was maintained around $\sim 60^{\circ}\text{C}$ by a temperature regulator. The bath containing the permeator was maintained at 40°C by another temperature regulator. The connecting lines between the humidifiers and the permeator as well as the constant temperature baths were properly insulated to reduce the heat loss. Even with these modifications, however, precise control of the system temperature was difficult.

The purification performance is reported in Table 4-27. The system operation was stable. The CO_2 composition in the purified gas stream varied from 3 to 7%. Such a variation can be explained by the temperature fluctuations in the system over the long period. Comparing the data of Table 4-27 with that of low temperature (25°C) run in Table 4-25, we see that a better quality of the purified gas stream was achieved. The gas permeation rate was certainly higher at higher temperature. However, the average N_2 recovery was lower. As temperature increases, the N_2 permeation rate also increases. Throughout the experiment, a slow increase in feed outlet flow rate was seen. This was probably due to a slow drying of the membrane liquid. To counteract this, membrane liquid recirculation with water addition from outside can be instituted. A better temperature and humidity control can be implemented for higher temperature runs.

Aqueous Solution of 20 wt% DEA as Liquid Membrane and 40% CO_2 - 60% CH_4 as Feed Gas

The simulated biogas mixture containing 40% CO_2 - 60% CH_4 was introduced at a pressure of 45 psig. Pure N_2 gas was used as sweep gas. Both gas streams were humidified. The flow rates of feed and sweep gas were 50 sccm and 200 sccm, respectively. Pure helium was used to pressurize the membrane liquid storage tank. Permeator #8 was used.

The experimental results of 12 hours' purification are shown in Figure 4-15. A steady performance was obtained in 6 hours. Simulation results and the steady

Table 4-27

PURIFICATION RUN AT HIGH TEMPERATURE WITH MODEL BIOGAS IN SWEEP GAS MODE
AND 20 WT% DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Sweep Side Flow Rate scc/min		Feed Side Pressure psig		Sweep Side Pressure psig		Feed Outlet Composition Percentage N ₂ /CO ₂ *		Sweep Outlet Composition Percentage N ₂ /CO ₂ *	
	Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		N ₂ /CO ₂ *		N ₂ /CO ₂ *	
3	50.0/24.29		200.0/223.43		45.0/44.9		9.4/2.0		70.60/20.32		4.46/7.18	
6	50.0/23.72		200.0/224.53		45.0/44.9		9.2/2.0		83.53/4.45		3.68/7.54	
9	50.0/23.89		200.0/224.64		45.0/44.9		9.0/2.0		83.94/2.83		3.42/7.60	
20	50.0/25.11		200.0/224.37		45.0/44.9		8.8/2.0		86.09/4.11		3.15/8.02	
21	50.0/25.14		200.0/224.34		45.0/44.9		8.2/2.0		85.69/4.15		3.15/8.05	
25	50.0/25.27		200.0/224.36		45.0/44.9		8.2/2.0		85.74/3.16		3.00/8.13	
27	50.0/25.32		200.0/223.70		45.0/44.9		8.0/2.0		85.79/2.71		2.90/7.92	
29	50.0/26.39		200.0/222.76		45.0/44.9		8.0/2.0		84.77/3.13		2.84/7.94	
43.5	50.0/26.53		200.0/222.97		45.0/44.9		8.0/2.0		91.50/5.20		2.94/8.58	
45.5	50.0/26.65		200.0/223.05		45.0/44.9		8.0/2.0		90.10/5.26		2.91/8.52	
47.5	50.0/26.81		200.0/222.40		45.0/44.9		8.0/2.0		89.70/4.35		2.85/8.27	
49	50.0/26.27		200.0/223.16		45.0/44.9		8.0/2.0		89.89/4.50		2.88/8.44	

Table 4-27 (cont.)

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *
50	50.0/26.49		200.0/222.84		45.0/44.9		8.0/2.0		92.85/4.63		2.90/8.73	
52	50.0/26.30		200.0/222.49		45.0/44.9		8.0/2.0		94.86/4.67		2.98/9.01	
55.5	50.0/26.24		200.0/222.10		45.0/44.9		8.0/2.0		91.01/3.99		2.86/8.55	
68	50.0/27.90		200.0/220.55		45.3/45.1		7.9/2.0		90.41/6.73		2.68/8.33	
70.5	50.0/27.20		200.0/222.35		46.0/45.1		8.0/2.0		88.49/5.96		2.62/8.47	
72.5	50.0/28.01		200.0/221.45		46.0/45.0		8.0/2.0		89.77/5.84		2.61/8.42	
76.5	50.0/28.08		200.0/220.43		46.0/45.1		8.0/2.0		91.51/4.85		2.61/8.49	
91	50.0/27.93		200.0/220.33		46.0/45.1		8.0/2.0		92.80/5.06		2.50/8.66	
94.5	50.0/28.87		200.0/219.67		46.0/45.1		8.0/2.0		91.08/6.49		2.39/8.44	
97	50.0/29.08		200.0/218.95		46.0/45.1		8.0/2.0		89.30/6.27		2.37/8.22	
100	50.0/29.70		200.0/218.79		46.0/45.1		8.0/2.0		82.61/6.61		2.24/7.53	

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 40°C; Sweep: Helium;
 Shell Press.: 50 psig; Shell liquid pressurized with helium;
 100% Humidified feed and sweep gas; Average N₂ Recovery: 79%

FIGURE 4-15
PERFORMANCE OF MODEL BIOGAS PURIFICATION WITH
AQUEOUS 20 WT% DEA SOLUTION AS MEMBRANE

state data are also compared in Table 4-28. The average CH_4 recovery was around 93%. The purified feed gas stream contained only 7% CO_2 . Note that, the effective permeation area in permeator #8 is around 30% of that of a 5-ft-long permeator (e.g., permeator #3 or #5). The permeation rate of sweep N_2 into feed stream was very low. The average N_2 concentration is around 2%.

These experiments demonstrate that both high purification and recovery can be simultaneously achieved in a small permeator when 20 wt% DEA in water is used as the liquid membrane. This is very encouraging because, unlike 30 wt% K_2CO_3 solution liquid membrane, the increased selectivity has been achieved without sacrificing the permeability to any extent.

Aqueous Solution of 10 wt% DEA as Liquid Membrane and 5% CO_2 - 95% N_2 as Feed Gas

Effect of partial pressure on CO_2 permeability was studied in HFCLM permeator #8 by using feed gas containing a lower percentage of CO_2 . Experiments were carried out with humidified feed and sweep gas streams. Feed gas was maintained at 45 psig in all the runs. Steady state data with 10 wt% DEA as liquid membrane are shown in Table 4-29. The data suggest much higher permeability of CO_2 compared to high pressure data (Table 4-21).

After completion of the separation run with DEA as liquid membrane, another experiment with pure water as liquid membrane has been carried using permeator #8. At first the permeator was cleaned with water and then dried with nitrogen gas. This was done in order to determine the effect, if any, of long-time DEA exposure of the permeator. Dry feed and sweep gas flow rates of 50 sccm and 200 sccm were used in this particular run. The data presented in Table 4-30 compare very well with the data taken earlier under identical conditions (4th row; Table 4-16). This implies that long-term exposure to the DEA solutions did not affect the microporous polypropylene hollow fibers at all.

Aqueous Solution of NMP as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas

Permeator #9 had been used for gas purification studies with 1-methyl-2-pyrrolidinone (NMP) solution as contained liquid membrane. First a solution

Table 4-28

PURIFICATION RUN UNDER SWEEP GAS MODE OF OPERATION WITH MODEL BIOGAS
AND 20 WT% DEA AS MEMBRANE IN PERMEATOR #8

Feed Side Flow Rate scc/min in/out	Sweep Side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep Side Pressure psig in/out	Feed Outlet Composition Percentage CH ₄ /CO ₂ *	Sweep Outlet Composition Percentage CH ₄ /CO ₂ *	Methane Recovery Percent- age
50.0/31.85	200.0/218.13	45.0/44.5	6.2/1.0	92.48/6.96	1.55/7.60	92.89
Simulation [†]						
50.0/29.14	200.0/220.86	45.0/44.8	6.2/1.0	91.22/6.63	1.55/8.18	88.62

* Balance Nitrogen; Feed: 40%CO₂-60%CH₄; Bath Temp.: 25°C; Sweep: Nitrogen;

Shell Press.: 50 psig; Membrane Liquid: 20 wt% DEA; 100% Humidified feed and sweep gas

[†]Permeability values used for different gas species are:

$$Q_{\text{CO}_2} = 96.0 \times 10^{-9} \text{ scc-cm}/(\text{cm}^2\text{-s-cm Hg}); Q_{\text{CH}_4} = 4.82 \times 10^{-9} \text{ scc-cm}/(\text{cm}^2\text{-s-cm Hg});$$

$$Q_{\text{N}_2} = 2.52 \times 10^{-9} \text{ scc-cm}/(\text{cm}^2\text{-s-cm Hg})$$

Table 4-29

STEADY STATE DATA AND SIMULATION RESULTS WITH 5% CO₂ - 95% N₂ FEED GAS
AND 10 WT% DEA AS MEMBRANE IN PERMEATOR #8

Feed Side Flow Rate scc/min Inlet/Outlet	Sweep Side Flow Rate scc/min Inlet/Outlet	Feed Side Pressure psig Inlet/Outlet	Sweep Side Pressure psig Inlet/Outlet	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *
Data					
50.0/46.21	200.0/204.13	45.0/44.2	6.0/1.0	93.29/0.0	1.55/1.17
75.0/69.95	200.0/207.5	45.0/44.2	6.1/1.0	95.51/0.54	1.58/1.73
100.0/93.09	200.0/210.83	45.0/44.0	6.2/1.0	95.31/0.91	1.47/2.20
100.0/94.79	300.0/308.56	45.0/44.0	8.2/1.0	94.91/0.73	0.96/1.40
Simulation ⁺					
50.0/46.48	200.0/203.52	45.0/44.7	6.1/1.0	94.9/0.10	1.67/1.21
75.0/70.52	200.0/204.48	45.0/44.5	6.1/1.0	96.22/0.40	1.66/1.70
100.0/94.77	200.0/205.23	45.0/44.3	6.1/1.0	96.67/0.78	1.65/2.08
100.0/94.90	300.0/305.10	45.0/44.3	8.2/1.0	96.54/0.74	1.11/1.41

* Balance Helium; Feed: 5%CO₂-95%N₂; Bath Temp.: 25°C; Sweep: Helium;

Shell Press.: 50 psig; 100% Humidified Feed and Sweep gas

⁺Permeability values used for different gas species are:

$$Q_{\text{CO}_2} = 220.0 \times 10^{-9} \text{ scc-cm}/(\text{cm}^2 \text{-s-cm Hg}); Q_{\text{N}_2} = 3.86 \times 10^{-9} \text{ scc-cm}/(\text{cm}^2 \text{-s-cm Hg});$$

$$Q_{\text{He}} = 9.045 \times 10^{-9} \text{ scc-cm}/(\text{cm}^2 \text{-s-cm Hg})$$

Table 4-30

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP GAS MODE
AND WATER AS MEMBRANE IN PERMEATOR #8

Elap- sed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage	N ₂ /CO ₂ *	Composition Percentage	N ₂ /CO ₂ *
2	50.0/30.96		200.0/218.11		45.0/44.1		10.0/2.0		76.67/15.01		2.42/8.08	
4	50.0/29.70		200.0/218.10		45.0/44.1		10.5/2.0		80.12/8.70		2.35/8.13	
6	50.0/29.53		200.0/218.14		45.0/44.1		10.4/2.0		83.24/7.68		2.37/8.09	
8	50.0/29.53		200.0/218.96		45.0/44.1		10.4/2.0		82.58/8.07		2.38/8.16	
11.5	50.0/29.03		200.0/218.10		45.0/44.1		10.6/2.0		83.22/7.60		2.36/8.13	
12.5	50.0/29.00		200.0/218.00		45.0/44.1		10.6/2.0		83.49/7.63		2.35/8.22	
24	50.0/29.78		200.0/219.10		45.0/44.1		10.7/2.0		81.84/7.11		2.25/8.18	
25	50.0/29.90		200.0/219.29		45.0/44.1		10.7/2.0		81.62/7.18		2.33/7.92	

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Non humidified feed and sweep gas; Average N₂ Recovery: 81.53%

containing 80 vol% NMP and 20 vol% water was tried as a liquid membrane. As Table 4-31 indicates, the level of purification was low (about 23% CO₂ in the purified gas stream). A slow and steady increase in sweep inlet pressure led us to believe that the membrane liquid was penetrating the pores of the microporous sweep fibers due to high pressure differential (ΔP) between the liquid membrane and the sweep gas stream. Therefore, after 5 hours, the sweep outlet pressure was raised from 2 psig to a level of 10 psig in order to reduce this pressure differential. The feed flow rate was also lowered. The reduction in feed flow rate resulted in a slightly better performance. However, the sweep gas pressure continued to increase slowly and after a period of time membrane liquid was clearly visible in the connecting lines of the sweep side and the experiment was discontinued.

After thorough washing and drying, the permeator was again used for gas purification studies. This time a liquid mixture having a lower NMP concentration was selected as a membrane liquid. The contained liquid membrane was made of 70 vol% NMP and 30 vol% water. The experiment was carried out at a lower pressure to begin with. A steady and stable performance was observed under these conditions, as shown in Table 4-32. The permeation rate of N₂ into the sweep stream was very low. The nitrogen recovery was about 92%. The CO₂ composition in the feed outlet was, however, relatively high (27%).

After 25 hours of experimental run, the feed as well as membrane liquid storage tank pressures were increased, keeping the feed and sweep flow rates the same. The run was continued for another 50 hours. A stable performance was again observed. The experimental results are reported in Table 4-33. The overall performance improved slightly due to a higher pressure of the feed stream. The CO₂ composition in the feed outlet dropped to about 24%. The nitrogen loss in the sweep stream was also very low.

These experiments suggest that stable performance is achievable with a membrane liquid having a composition of 70 vol% NMP and 30 vol% water. Very high nitrogen recovery was obtained when NMP solution was used as a liquid membrane, but the level of purification was low compared to the other membrane liquids we have studied.

Table 4-31

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP GAS MODE
AND 80 VOL% NMP SOLUTION AS MEMBRANE IN PERMEATOR #9

Elapsed Time hrs.	Feed Side Flow Rate scc/min Inlet/Outlet	Sweep Side Flow Rate scc/min Inlet/Outlet	Feed Side Pressure psig Inlet/Outlet	Sweep Side Pressure psig Inlet/Outlet	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *
2	100.0/75.31	200.0/226.90	45.0/44.0	9.1/2.0	74.05/20.95	0.90/9.77
3	100.0/76.53	200.0/225.50	45.0/44.0	10.0/2.0	72.72/22.26	0.88/9.31
4	100.0/77.40	200.0/224.98	45.0/44.0	10.5/2.0	71.56/23.19	0.81/8.94
5	100.0/77.35	200.0/224.44	45.0/44.0	10.5/2.0	71.80/23.14	0.81/8.99 ⁺
Feed flow rate and sweep outlet pressure were changed						
7	50.0/34.40	200.0/216.95	45.0/44.5	16.7/10.0	74.92/18.66	0.77/6.49
9	50.0/33.78	200.0/216.13	45.0/44.7	17.1/10.0	77.31/15.42	0.75/6.35
10	50.0/34.22	200.0/214.76	44.9/44.7	17.3/10.0	77.41/15.65	0.77/6.26
22	50.0/34.46	200.0/215.51	45.0/44.5	18.5/10.0	76.50/17.37	0.68/6.05
23	50.0/34.47	200.0/215.81	45.0/44.5	18.6/10.0	75.93/17.68	0.73/6.21
25	50.0/34.50	200.0/215.39	45.0/44.5	18.8/10.0	75.13/17.40	0.71/6.15 ⁺⁺

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Shell liquid pressurized with helium;
100% Humidified feed and sweep gas; Average N₂ Recovery: ⁺ 92.6%; ⁺⁺ 87.6%

Table 4-32

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP GAS MODE
AND 70 VOL% NMP SOLUTION AS MEMBRANE IN PERMEATOR #9

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage	N ₂ /CO ₂ *	Composition Percentage	N ₂ /CO ₂ *
1	50.0/39.34		200.0/206.75		25.25/24.0		7.7/2.0		69.77/27.42		0.50/4.15	
2	50.0/39.45		200.0/207.73		25.25/25.0		7.7/2.0		70.17/26.75		0.47/4.17	
3	50.0/39.45		200.0/207.77		25.25/24.9		7.7/2.0		70.37/26.61		0.42/4.16	
4	50.0/39.43		200.0/207.32		25.25/25.0		7.6/2.0		70.46/26.65		0.42/4.11	
5	50.0/39.44		200.0/207.83		25.25/24.9		7.6/2.0		70.38/26.67		0.40/4.11	
6.5	50.0/39.93		200.0/207.81		25.25/25.0		7.8/2.0		70.38/26.62		0.44/4.10	
8	50.0/39.46		200.0/206.78		25.25/25.0		7.8/2.0		70.10/26.74		0.41/4.18	
20	50.0/38.91		200.0/205.87		25.25/25.0		8.0/2.0		70.42/26.86		0.33/4.16	
21	50.0/38.87		200.0/205.89		25.25/24.9		8.0/2.0		70.74/26.80		0.35/4.12	
23	50.0/38.95		200.0/205.92		25.25/24.9		7.9/2.0		70.07/26.90		0.34/4.09	
25	50.0/39.29		200.0/206.86		25.40/24.9		7.9/2.0		70.45/27.18		0.34/4.13	

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 28 psig; Shell liquid pressurized with helium;
100% Humidified feed and sweep gas; Average N₂ Recovery: 92.3%

Table 4-33

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP GAS MODE
AND 70 VOL% NMP SOLUTION AS MEMBRANE IN PERMEATOR #9

Elapsed Time hrs.	Feed Side Flow Rate scc/min Inlet/Outlet	Sweep Side Flow Rate scc/min Inlet/Outlet	Feed Side Pressure psig Inlet/Outlet	Sweep Side Pressure psig Inlet/Outlet	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *
1	50.0/38.33	200.0/209.80	45.0/44.2	8.2/2.0	67.11/31.17	0.51/5.03
3	50.0/37.31	200.0/210.76	45.0/44.2	8.5/2.0	73.72/23.52	0.55/5.03
4.5	50.0/37.28	200.0/209.69	45.0/44.3	8.2/2.0	73.67/23.71	0.59/5.10
19	50.0/36.37	200.0/210.73	45.0/44.3	8.0/2.0	74.30/23.12	0.65/5.00
20	50.0/36.79	200.0/210.74	45.0/44.3	7.8/2.0	74.16/23.43	0.55/5.05
21.5	50.0/36.79	200.0/210.77	45.0/44.3	7.8/2.0	73.89/23.60	0.55/5.02
24.5	50.0/36.82	200.0/211.01	45.0/44.3	7.8/2.0	74.19/23.29	0.70/5.08
29.5	50.0/36.47	200.0/211.42	45.0/44.3	8.1/2.0	74.37/22.63	0.75/5.22
43.5	50.0/38.43	200.0/208.53	45.0/44.3	8.0/2.0	72.89/25.30	0.33/4.44
46.5	50.0/37.60	200.0/210.05	45.0/44.3	8.5/2.0	73.12/24.66	0.51/4.78
48.5	50.0/37.65	200.0/209.94	45.0/44.5	8.4/2.0	73.57/24.17	0.55/4.87
49.5	50.0/37.64	200.0/209.99	45.0/44.5	8.4/2.0	73.94/23.99	0.51/4.85

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Shell liquid pressurized with helium;
100% Humidified feed and sweep gas; Average N₂ Recovery: 92.2%

PURIFICATION STUDIES OF MODEL BIOGAS MIXTURES IN CONVENTIONAL POLYMERIC MEMBRANE MODE WITH DIFFERENT LIQUID MEMBRANES

Model biogas purification in a HFCLM permeator, operated in the conventional polymeric membrane mode, was carried out as follows. Model feed biogas mixture consisting of 40% CO₂ - 60% N₂ was introduced through one set of fibers at an inlet pressure of 45 psig. No sweep gas or vacuum was applied through the other set. The necessary permeate pressure was built up by the permeated gas itself. The particular permeate end, which was earlier used for sweep gas introduction, was kept closed to maintain a countercurrent flow of the permeate stream.

Water as Liquid Membrane and 40% CO₂ - 60% N₂ as Feed Gas

Results obtained at five different flow rates in permeator #3 are reported in Table 4-34. Note that, at the lowest feed flow rate of 50 sccm, the purified feed gas stream contained only about 5% CO₂. However, the nitrogen recovery in this case was around 70%. The data and the simulation results are plotted in Figure 4-16. The simulation results are in very good agreement with the experimental data.

The same data are presented in a different way in Figure 4-17, where a plot of stage cut (ratio of the permeate flow rate to the feed flow rate) against mole fractions of N₂ and CO₂ in feed outlet stream (commonly known as reject stream) is shown. As usual an increase in stage cut increases N₂ in the reject stream and improves the quality of the purified gas.

Similar type of experiments were carried out using permeator #6. Here, the permeate gas was withdrawn through the larger bore fibers. Steady state results are reported in Table 4-35. Even though a very high percentage of nitrogen was recovered in these experiments, the extent of feed purification was low. For example, at the lowest feed flow rate of 50 sccm, the purified gas stream contains about 20% CO₂. This performance is reasonably good when we consider that permeator #6 is only 2 feet long and the membrane area in permeator #6 is only 40% that of permeator #3. The data and the numerical simulation results are shown in Figure 4-18. The model predicts the performance quite well.

Table 4-34

PURIFICATION RUNS UNDER CONVENTIONAL MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #3

Feed Side Flow Rate scc/min in/out	Permeate Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Permeate Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂	Nitrogen Recovery Percent- age
50.0/22.18	0.0/27.59	45.0/43.5	6.7/2.0	97.78/5.28	40.97/61.00	71.55
100.0/59.23	0.0/40.74	45.0/41.3	7.2/2.0	87.21/13.89	27.71/73.13	86.09
150.0/102.55	0.0/46.95	45.0/40.0	8.0/2.0	80.68/20.88	23.38/77.88	91.93
200.0/149.36	0.0/49.97	45.0/40.0	8.5/2.0	75.82/25.75	21.20/80.14	94.51
250.0/195.04	0.0/51.88	45.0/36.0	8.7/2.0	73.90/27.92	19.62/81.92	96.09

Feed: 40% CO₂-60% N₂; Shell Press.: 50 psig; Membrane Liquid: Water; Bath Temp.: 25°C

FIGURE 4-16
 FEED FLOW VARIATION STUDIES: CONVENTIONAL
 POLYMERIC MEMBRANE MODE OF OPERATION IN PERMEATOR #3

FIGURE 4-17
 SEPARATION UNDER CONVENTIONAL POLYMERIC
 MEMBRANE MODE: STAGE CUT VS. COMPOSITION IN PERMEATOR #3

Table 4-35

PURIFICATION RUNS UNDER CONVENTIONAL MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #6

Feed Side Flow Rate scc/min in/out	Permeate Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Permeate Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂	Nitrogen Recovery Percent- age
50.0/34.11	0.0/16.75	45.0/44.0	1.5/0.5	81.79/19.02	20.85/79.54	93.0
100.0/78.47	0.0/22.96	45.0/43.2	1.7/0.5	74.86/26.03	15.50/84.81	97.9
150.0/125.56	0.0/26.40	45.0/42.3	2.0/0.6	71.19/30.37	15.06/85.41	99.3
200.0/172.15	0.0/28.98	45.0/42.3	2.5/0.6	69.41/32.06	13.53/87.23	99.6

Feed: 40% CO₂-60% N₂; Shell Press.: 50 psig; Membrane Liquid: Water; Bath Temp.: 25°C

FIGURE 4-18
 FEED FLOW VARIATION STUDIES: CONVENTIONAL
 POLYMERIC MEMBRANE MODE OF OPERATION IN PERMEATOR #6

The data for the permeator #8 is shown in Table 4-36. The purified gas stream at 50 sccm flow rate contains about 20% CO₂. Note that, the effective length of permeator #8 is around 30% that of permeator #3. Experimental data and numerical simulation results are shown in Figure 4-19. Although, permeator #8 has smaller membrane area than permeator #6, a similar quality in the purified gas was obtained due to a lower effective liquid membrane thickness in permeator #8. The deviation in the permeate composition (CO₂/P and N₂/P) was due to leakage of air into the permeate stream which was diluted with respect to CO₂ content. Since it occurred beyond the flow meter it did not affect the permeation process which is evident from the very good prediction of the performance of the feed side compared to permeate side.

Separation runs with permeator #3 were also carried out in a fashion somewhat different from the conventional mode of operation; both ends of the permeate fibers were kept open. The permeate flow was cocurrent-countercurrent in nature. Pure water was used as membrane liquid. This mode was identified as the split permeation mode (Majumdar, 1982). The steady state results for five different flow rates are shown in Table 4-37. Figure 4-20 shows the corresponding plot. Comparing the data with those obtained with conventional mode of operation (Table 4-34), it is clear that the overall permeation rate is considerably higher in split permeation mode of operation. The higher permeation rate is a result of an increase in driving force across the liquid membrane, which arises due to a reduction in permeate fiber lumen pressure drop. However, the quality of the purified stream is not necessarily better in this case. At lower feed flow rates, the nitrogen content in the purified gas stream is slightly lower in the present mode of operation and the same is marginally higher at high flow rates. At higher flow rates, the effect of a reduction in the permeate fiber lumen pressure drop resulted in an improved performance.

30 wt% K₂CO₃ Solution as Liquid Membrane and 40% CO₂ - 60% N₂ as Feed Gas

Separation of model biogas mixture was also carried out under conventional mode of operation with 30 wt% K₂CO₃ solution as liquid membrane in permeator #5. The experiments were conducted at four different flow rates e.g., 50, 75, 100 and 150 sccm. The steady state data are presented in Table 4-38. Feed inlet

Table 4-36

PURIFICATION RUNS UNDER CONVENTIONAL MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #8

Feed Side Flow Rate scc/min in/out	Permeate Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Permeate Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂	Nitrogen Recovery Percent- age
50.0/27.11	0.0/25.52	45.2/44.5	2.7/2.0	82.19/19.80	37.63/64.37	74.3
75.0/48.43	0.0/27.54	45.0/44.0	2.7/2.0	78.84/23.86	32.33/69.47	84.87
100.0/71.53	0.0/31.43	45.0/44.0	2.75/2.0	74.94/26.83	27.72/74.07	89.35

Feed: 40% CO₂-60% N₂; Shell Press.: 50 psig; Membrane Liquid: Water; Bath Temp.: 25°C

FIGURE 4-19
 FEED FLOW VARIATION STUDIES: CONVENTIONAL
 POLYMERIC MEMBRANE MODE OF OPERATION IN PERMEATOR #8

Table 4-37

PURIFICATION RUNS UNDER SPLIT PERMEATION MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #3

Feed Side Flow Rate scc/min in/out	Permeate Flow Rate scc/min out	Feed Side Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂	Nitrogen Recovery Percent- age
50.0/20.47	13.69/17.39	45.0/43.5	89.86/10.94	66.03/34.66	24.81/75.79 61.30
100.0/58.42	19.65/23.37	45.0/41.5	83.56/17.54	45.64/54.94	18.40/82.54 81.35
150.0/100.19	22.06/28.56	45.0/39.8	79.62/22.03	35.80/64.22	16.38/84.91 88.46
200.0/143.56	23.85/32.63	45.2/38.0	76.59/24.95	30.79/68.19	15.33/85.85 91.63
250.0/184.76	24.72/39.30	45.2/37.5	75.0/25.90	27.63/70.28	14.10/86.44 92.38

Feed: 40% CO₂-60% N₂; Shell Press.: 50 psig; Membrane Liquid: Water; Bath Temp.: 25°C;
Both the permeate side pressures were maintained at 2 psig;
‡ Cocurrent side
* Countercurrent side

FIGURE 4-20
FEED FLOW VARIATION STUDIES: SPLIT
PERMEATION MODE OF OPERATION IN PERMEATOR #3

Table 4-38

SIMULATION RESULTS AND STEADY STATE DATA UNDER CONVENTIONAL MODE OF OPERATION
WITH MODEL BIOGAS AND 30 WT% K₂CO₃ SOLUTION AS MEMBRANE IN PERMEATOR #5

Feed Side Flow Rate scc/min in/out	Permeate Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Permeate Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂	Nitrogen Recovery Percent- age
Data						
50.0/42.41	0.0/9.31	44.75/43.7	2.5/1.0	69.84/30.39	20.60/79.92	93.61
75.0/67.63	0.0/11.56	45.0/43.3	2.5/1.0	68.81/31.83	17.36/82.72	95.54
100.0/90.0	0.0/12.10	45.0/43.0	2.5/1.0	67.61/33.67	14.92/85.62	96.99
150.0/138.93	0.0/14.23	45.5/41.7	2.7/1.0	65.05/35.05	12.94/86.87	97.95
Simulation [†]						
50.0/38.91	0.0/11.09	45.0/43.98	1.38/1.0	73.11/26.89	14.01/85.99	94.82
75.0/62.89	0.0/12.11	45.0/43.41	1.43/1.0	69.15/30.85	12.48/87.52	96.64
100.0/87.38	0.0/12.62	45.0/42.82	1.46/1.0	66.96/33.04	11.75/88.25	97.53
150.0/136.98	0.0/13.02	45.0/41.63	1.48/1.0	64.65/35.35	11.10/88.90	98.39

Feed: 40% CO₂-60% N₂; Shell Press.: 50 psig; Membrane Liquid: 30 wt% K₂CO₃ solution
100% humidified feed gas; Bath Temp.: 25°C;

[†] Permeability values used for different gas species are:

$$Q_{\text{CO}_2} = 24.0 \times 10^{-9} \text{ scc-cm}/(\text{cm}^2\text{-s-cm Hg}); Q_{\text{N}_2} = 0.682 \times 10^{-9} \text{ scc-cm}/(\text{cm}^2\text{-s-cm Hg});$$

$$Q_{\text{He}} = 1.192 \times 10^{-9} \text{ scc-cm}/(\text{cm}^2\text{-s-cm Hg})$$

pressure of 45 psig was maintained in all the cases. Nitrogen recovery was very high, but the extent of feed gas purification was quite low in such mode. The CO_2 composition in the feed outlet was very high and it increased with an increase in feed flow rate. This is due to the significantly lower permeability values of the gases through the salt solution at 25°C . The steady state data and numerical results for the same conditions are compared in Table 4-38 and graphically demonstrated in Figure 4-21. A plot of stage cut vs composition is shown in Figure 4-22. Note that the simulation was based on permeability of CO_2 with no facilitation. This is expected as the partial pressure driving force is drastically reduced in this mode and the carrier in the membrane liquid gets saturated. Moreover, there may be slow fouling of the microporous hollow fibers by microcrystals of salt.

PURIFICATION STUDIES OF MODEL BIOGAS MIXTURES UNDER VACUUM MODE OF OPERATION

Model biogas purification studies under vacuum mode of operation were carried out mainly with pure water as a liquid membrane. Either 40% CO_2 - 60% N_2 or 40% CO_2 - 60% CH_4 was used as a feed gas. In all experiments with water membrane, the feed gas stream was introduced without any humidification. Two separation experiments were carried out with 7 wt% K_2CO_3 solution as a contained liquid membrane.

Water as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas

Experimental data were taken at three different feed pressures using permeator #3. The steady state data at feed pressures 30, 35 and 40 psig are reported in Table 4-39. Three different feed gas flow rates (e.g., 100, 150 and 200 sccm) were used in each case. The above experimental data as well as results from numerical simulation of the model are plotted in Figures 4-23, 4-24 and 4-25, respectively.

As expected, the CO_2 content in the purified gas increased with an increase in feed flow rate. At a low feed flow rate of 100 sccm, the CO_2 percentage in the purified gas was found to be 3-4%. A comparison of the data in these three tables reveals that, at any fixed value of flow rate, the stage cut (ratio of the permeate flow rate to the feed flow rate) increased with an increase in

FIGURE 4-21
FEED FLOW VARIATION STUDIES: CONVENTIONAL
POLYMERIC MEMBRANE MODE OF OPERATION IN PERMEATOR #5

FIGURE 4-22
 SEPARATION UNDER CONVENTIONAL POLYMERIC
 MEMBRANE MODE: STAGE CUT VS. COMPOSITION IN PERMEATOR #5

Table 4-39

PURIFICATION RUNS UNDER VACUUM MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #3

Shell Pres- sure psig	Feed Side Flow Rate scc/min in/out	Permeate Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Permeate Pressure in of Hg in/out	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂	Nitrogen Recovery Percent- age
35	100/52.30	0/48.43	30.0/26.2	17.0/0.7	95.58/3.46	23.17/75.07	83.31
	150/61.85	0/61.85	30.0/22.5	18.0/0.2	88.91/11.19	18.20/81.34	88.98
	200/127.55	0/72.46	30.0/22.0	18.0/0.7	85.81/13.75	14.54/83.77	91.21
40	100/51.53	0/49.34	35.5/31.5	18.0/0.3	96.19/3.84	25.76/73.52	82.61
	150/86.19	0/66.0	35.0/27.6	19.0/0.3	91.22/8.83	19.38/80.14	87.36
	200/123.2	0/78.53	35.0/26.0	20.0/0.7	87.31/12.19	15.78/82.76	89.64
45	100/49.73	0/51.41	40.0/37.0	18.4/0.7	97.11/3.07	27.25/72.30	80.49
	150/86.19	0/66.0	40.3/34.0	18.5/0.3	93.83/6.53	20.24/79.47	89.96
	200/120.78	0/81.10	40.3/35.0	20.6/0.7	89.07/10.84	17.83/82.08	89.65

Feed: 40% CO₂-60% N₂; Membrane Liquid: Water; Bath Temp.: 25°C

FIGURE 4-23
 FEED FLOW VARIATION STUDIES:
 VACUUM MODE OF OPERATION IN PERMEATOR #3

FIGURE 4-24
FEED FLOW VARIATION STUDIES:
VACUUM MODE OF OPERATION IN PERMEATOR #3

FIGURE 4-25
 FEED FLOW VARIATION STUDIES:
 VACUUM MODE OF OPERATION IN PERMEATOR #3

feed pressure.

To illustrate the feed pressure effect on separation more clearly, the above three figures are combined in the Figure 4-26. It is evident that higher feed pressure improves the quality of the purified biogas. The simulation results appear to describe the behavior quite well. The CO_2 content in the feed outlet is somewhat underpredicted. That is especially true for 40 psig feed pressure.

Similar experiments under vacuum mode of operation were also carried out with permeator #5. Permeators #3 and #5 contain equal number of hollow fibers of identical size and length. However, there is no extra shell space around the fiber bundle in permeator #5. Feed inlet pressures of 30 and 35 psig were maintained during the experimental runs. The steady state data, obtained by varying the feed flow rates, are reported in Table 4-40.

The experimental data and numerical simulations for feed pressures of 30 psig and 35 psig are shown in Figures 4-27 and 4-28, respectively. The conclusions drawn earlier for permeator #3 are also valid in this case. The simulation results, in general, agree with the data. The simulation results for permeator #3 are also valid for permeator #5 because the effective liquid membrane thicknesses in these two permeators are considered equal.

The performance data for the mixed fiber permeator #6 are reported in Table 4-41. Vacuum was pulled through the larger fiber set and the permeate gas flow was countercurrent to the feed gas flow. The data for these three different feed pressures are plotted in Figures 4-29, 4-30 and 4-31, respectively. The numerical simulations were carried out with a membrane thickness of 0.01 inch. Here again, we notice that the stage cut increased with a decrease in pressure ratio (ratio of permeate pressure to the feed pressure). At a low feed flow rate (e.g., 50 sccm; feed pressure 35 psig) the purified gas stream contained about 11% CO_2 . This performance is reasonably good when we consider that permeator #6 is only 2 ft long and the membrane area in permeator #6 is only 40% of that of permeators #3 or #5.

The vacuum purification data for permeator #8 with pure water as liquid membrane is given in Table 4-42. The data and the numerical results are plotted

FIGURE 4-26
 FEED FLOW AND PRESSURE VARIATION STUDIES:
 VACUUM MODE OF OPERATION IN PERMEATOR #3

Table 4-40

PURIFICATION RUNS UNDER VACUUM MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #5

Shell Pres- sure psig	Feed Side Flow Rate scc/min in/out	Permeate Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Permeate Pressure in of Hg in/out	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂	Nitrogen Recovery Percent- age
35.0	100/53.59	0/56.89	30.3/26.2	14.50/0.8	94.02/6.05	26.38/72.72	83.97
	150/93.63	0/60.44	30.0/23.5	15.93/0.3	88.64/12.75	20.83/79.59	92.21
	200/132.78	0/69.10	30.0/22.6	16.58/0.3	85.24/16.34	17.34/83.19	94.32
40.0	100/52.54	0/56.66	35.0/32.2	14.54/0.5	97.53/3.57	31.40/68.13	85.40
	150/87.68	0/65.63	35.0/30.5	16.10/0.3	93.40/8.68	21.37/79.73	90.99
	200/127.58	0/75.47	35.0/28.6	17.10/0.3	88.18/13.77	17.99/82.88	93.75

Feed: 40% CO₂-60% N₂; Membrane Liquid: Water; Bath Temp.: 25°C

FIGURE 4-27
 FEED FLOW VARIATION STUDIES:
 VACUUM MODE OF OPERATION IN PERMEATOR #5

FIGURE 4-28
FEED FLOW VARIATION STUDIES:
VACUUM MODE OF OPERATION IN PERMEATOR #5

Table 4-41

PURIFICATION RUNS UNDER VACUUM MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #6

Shell Pres- sure psig	Feed Side Flow Rate scc/min in/out	Permeate Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Permeate Pressure in of Hg in/out	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂	Nitrogen Recovery Percent- age
25	50/31.61 75/54.49 100/70.88	0/19.61 0/22.51 0/31.05	21.7/18.5 22.5/18.0 22.0/18.8	3.1/1.2 3.2/1.3 3.4/1.2	84.43/16.69 78.23/22.94 80.76/21.11	22.89/77.45 19.45/81.18 15.96/85.33	89.0 94.7 95.4
35	50/25.22 100/66.33 150/100.44	0/24.76 0/33.68 0/47.81	30.5/28.0 31.5/27.0 31.0/27.0	3.8/1.2 4.4/1.3 5.5/1.8	90.65/11.57 80.31/21.71 77.89/23.12	30.43/71.30 22.78/78.79 24.24/76.23	76.2 88.8 86.9
40	50/26.38 75/46.84 100/65.49	0/22.49 0/27.11 0/34.26	35.5/33.0 36.5/33.0 36.5/33.2	4.2/1.3 4.3/1.3 4.7/1.7	90.20/11.34 85.71/15.97 83.24/19.92	18.72/82.07 14.95/86.10 12.53/87.98	79.3 89.2 90.8

Feed: 40% CO₂-60% N₂; Membrane Liquid: Water; Bath Temp.: 25°C

FIGURE 4-29
FEED FLOW VARIATION STUDIES:
VACUUM MODE OF OPERATION IN PERMEATOR #6

FIGURE 4-30
FEED FLOW VARIATION STUDIES:
VACUUM MODE OF OPERATION IN PERMEATOR #6

FIGURE 4-31
 FEED FLOW VARIATION STUDIES:
 VACUUM MODE OF OPERATION IN PERMEATOR #6

Table 4-42

PURIFICATION RUNS UNDER VACUUM MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN PERMEATOR #8

Feed Side Flow Rate scc/min in/out	Permeate Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Permeate Pressure in of Hg in/out	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂	Nitrogen Recovery Percent- age
50.0/25.53	0.0/25.22	30.0/29.5	5.2/1.1	92.31/9.56	28.71/73.52	78.57
75.0/44.08	0.0/32.71	29.9/29.1	6.0/1.1	88.43/13.10	22.80/79.13	86.62
100.0/62.48	0.0/38.86	30.0/29.0	6.6/1.1	85.23/16.12	20.54/81.07	88.76
Feed: 40% CO ₂ -60% N ₂ ; Shell Press.: 35 psig; Membrane Liquid: Water; Bath Temp.: 25°C						

in Figure 4-32. The numerical results were obtained with a membrane thickness value of 0.00485 inch. The performance of permeator #8 was better than that of the mixed fiber permeator #6. For example, in case of permeator #8 with 100 sccm feed flow rate, we found about 16% CO_2 in the purified biogas stream whereas, under identical conditions, the CO_2 composition in the purified gas stream was about 22% when permeator #6 was used. Note further that, permeator #8 has smaller membrane area than permeator #6. The better performance of permeator #8 was most likely due to a lower effective liquid membrane thickness in permeator #8. The reduction in pressure drop in the large bore permeate fibers apparently has very limited effect for high feed gas pressure situations in the vacuum mode.

In order to explore liquid membrane stability under the vacuum mode of operation, a few long-term experiments were also carried out. Table 4-43 shows such a run carried out with permeator #3. Steady state was achieved within a period of 3-4 hrs. and all the parameters were maintained constant over the 26-hr. period after which the feed flow rate was changed to 150 sccm. Results of a similar experiment, carried out with permeator #5, are reported in Table 4-44 and the performance is shown in Figure 4-33. The purified gas stream showed only 3.5% CO_2 and remained constant for the entire period. The nitrogen recovery was about 85%.

In all such experiments, vacuum was pulled through one end of the permeate fibers while the other end was closed. In a variation of this simple vacuum mode, vacuum was pulled through the both ends of the permeate fibers of permeator #5. This mode was identified as split vacuum mode (Majumdar, 1982; Sengupta and Sirkar, 1986). The stable behavior is shown in Table 4-45. The data also show a slight improvement in permeation rate and quality of the purified gas compared to the simple vacuum mode operation (3rd row; Table 4-40).

Water as Liquid Membrane and 40% CO_2 - 60% CH_4 as Feed Gas

Long-term purification study of a CO_2 - CH_4 feed gas mixture was made under vacuum mode of operation using permeators #6 and #7, connected in series. The feed inlet flow rate was initially maintained at 75 sccm. The results are

FIGURE 4-32
 FEED FLOW VARIATION STUDIES:
 VACUUM MODE OF OPERATION IN PERMEATOR #8

Table 4-43

MODEL BIOGAS PURIFICATION STUDIES UNDER VACUUM MODE WITH WATER
AS LIQUID MEMBRANE IN PERMEATOR #3

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Permeate Flow Rate scc/min		Feed Side Pressure psig		Permeate Pressure in of Hg		Feed Outlet Composition Percentage N ₂ /CO ₂		Permeate Composition Percentage N ₂ /CO ₂	
	Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		Inlet/Outlet					
1	100.0/52.06		0.0/48.78		35.0/31.6		18.1/0.2		94.56/4.78		25.60/73.21	
4	100.0/51.58		0.0/49.42		35.5/31.6		18.4/0.2		94.99/4.46		25.99/72.95	
7	100.0/51.62		0.0/49.18		35.5/31.5		17.4/0.2		95.43/4.04		25.87/73.02	
10	100.0/51.03		0.0/49.10		35.5/31.5		17.9/0.2		95.99/3.99		25.86/73.82	
14	100.0/51.53		0.0/49.34		35.5/31.5		17.9/0.2		96.19/3.84		25.76/73.52	
16	100.0/51.55		0.0/49.26		35.3/31.0		17.9/0.2		95.96/3.96		25.41/73.91	
20	100.0/51.50				35.5/31.0		15.9/0.2		96.89/3.50			
25	100.0/51.54		0.0/49.02		35.5/31.0		16.9/0.2		97.12/3.22		25.09/74.53	
**27	150.0/84.53				40.0/34.0		18.4/0.2		93.57/6.78			
30	150.0/83.48		0.0/66.96		40.2/34.0		18.4/0.2		93.80/6.76		20.25/79.61	
31	150.0/83.52				40.2/34.0		18.4/0.2		93.59/6.81			
32	150.0/83.10		0.0/67.11		40.2/34.0		18.4/0.2		93.83/6.53		20.24/79.47	
33	150.0/82.58				40.2/34.0		18.4/0.2		93.83/6.53			

Feed: 40% CO₂-60% CO₂; Shell Press.: 40 psig; Membrane Liquid: Water; Bath Temp.: 25°C;
Shell pressure was raised to 45 psig.

Table 4-44

MODEL BIOGAS PURIFICATION STUDIES UNDER VACUUM MODE WITH WATER
AS LIQUID MEMBRANE IN PERMEATOR #5

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Permeate Flow Rate scc/min		Feed Side Pressure psig		Permeate Pressure in of Hg		Feed Outlet Composition Percentage N ₂ /CO ₂		Permeate Composition Percentage N ₂ /CO ₂ *	
	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	N ₂ /CO ₂	N ₂ /CO ₂	N ₂ /CO ₂ *	N ₂ /CO ₂ *
3.5	100.0/51.51	0.0/60.24	35.0/32.5	14.2/0.3	98.55/3.18	43.26/58.21						
5.5	100.0/52.06	0.0/59.78	35.0/32.5	14.2/0.3	98.43/3.30	43.05/58.42						
7.5	100.0/52.05	0.0/59.42	35.0/32.5	13.8/0.3	98.30/3.60	37.30/64.11						
9.5	100.0/52.99	0.0/59.02	35.0/32.5	13.9/0.3	98.32/3.40	36.98/63.81						
22	100.0/52.52	0.0/59.70	35.0/32.5	14.8/0.3	98.30/3.46	35.66/65.03						
24	100.0/52.36	0.0/59.88	35.0/32.5	13.9/0.4	98.11/3.37	35.09/65.51						
26	100.0/52.36	0.0/59.52	35.0/32.5	13.9/0.4	98.07/3.42	34.44/65.84						
28	100.0/52.36	0.0/59.35	35.0/32.5	13.8/0.4	97.98/3.52	34.08/66.22						
30	100.0/52.35		35.0/32.2	13.8/0.4	98.0/3.48							
32	100.0/52.38	0.0/58.14	35.0/32.2	13.7/0.4	98.06/3.48	33.37/67.02						
34	100.0/51.67		35.0/32.2	13.9/0.4	97.79/3.30							
36	100.0/52.38	0.0/57.14	35.0/32.2	13.9/0.4	98.06/3.48	33.37/67.02						
38	100.0/51.67		35.0/32.2	15.0/0.5	97.79/3.30							
46.5	100.0/53.16		35.0/32.2	15.0/0.5	97.50/3.64							
47.5	100.0/53.06	0.0/56.82	35.0/32.2	13.9/0.5	97.11/3.90	31.58/68.5						
49.5	100.0/52.66		35.0/32.2	14.4/0.5	97.62/3.48							
50.5	100.0/52.16	0.0/56.49	35.0/32.2	14.4/0.5	97.61/3.51	31.21/67.77						

Feed: 40% CO₂-60% CO₂; Shell Press.: 40 psig; Membrane Liquid: Water; Bath Temp.: 25°C;
Average nitrogen recovery: 84.85%;

*Leakage was found in the vacuum controlling valve located outside the permeator and it was detected after the experiment. However, it did not affect the feed outlet composition and flow rate.

FIGURE 4-33
 CLM STABILITY STUDIES: VACUUM MODE OF OPERATION
 WITH WATER AS MEMBRANE IN PERMEATOR #5

Table 4-45

MODEL BIOGAS PURIFICATION STUDIES UNDER SPLIT VACUUM MODE WITH WATER
AS LIQUID MEMBRANE IN PERMEATOR #5

Elapsed Time hrs.	Feed Side Flow Rate scc/min Inlet/Outlet	Permeate Flow Rate scc/min	Feed Side Pressure psig Inlet/Outlet	Permeate Pressure in of Hg	Feed Outlet Composition Percentage N ₂ /CO ₂	Permeate Composition Percentage N ₂ /CO ₂
2	200.0/120.78	91.74	35.4/29.8	0.5	90.57/9.91	40.81/58.47
4	200.0/119.73	90.90	35.0/29.0	0.5	90.31/10.19	28.66/70.45
6.5	200.0/120.03	90.09	35.2/29.0	0.5	90.51/10.25	25.41/73.89
8.5	200.0/121.20	87.72	35.2/29.0	0.5	90.68/10.22	25.74/75.32
10.5	200.0/121.39	87.34	35.2/29.0	0.5	90.84/10.21	25.67/75.43
13	200.0/120.73	87.72	35.25/29.0	0.5	90.76/10.14	25.88/75.25
23.5	200.0/120.77	86.96	35.5/29.0	0.6	89.97/10.68	25.53/75.16
26	200.0/120.93	86.96	35.5/29.0	0.6	90.26/10.48	25.32/75.57

Feed: 40% CO₂-60% CO₂; Shell Press.: 40 psig; Membrane Liquid: Water; Bath Temp.: 25°C;
Average Nitrogen Recovery: 90.76%

presented in Table 4-46 and in Figure 4-34. The average CH_4 recovery for this feed flow rate (75 sccm) was 85.3%. The CO_2 composition in the purified gas stream was about 13%. The results also show very little pressure drop in the permeate side. Note that, vacuum was applied through the set of fibers with a larger diameter. After 24 hours of experimental run, the feed gas flow rate was changed to 60 sccm. This produced a slightly higher CH_4 composition (~90%) at the purified gas end.

The above set of experiments suggest unequivocally that a trouble-free operation is possible with vacuum mode operation when pure water is utilized as a liquid membrane.

7 wt% K_2CO_3 Solution as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas

In the next two Tables 4-47 and 4-48, the vacuum purification performances with 7% K_2CO_3 solution are illustrated. The first set of data were taken with permeator #3 which has a large shell space around the fiber bundle. Here, the feed outlet behavior with respect to CO_2 showed some unsteadiness. This unsteadiness was somewhat eliminated when permeator #4 was used (Table 4-48). However, the quality of the purified gas was poor even when the feed flow rate was reduced to a lower value of 50 sccm (Table 4-48).

PURIFICATION STUDIES OF MODEL BIOGAS MIXTURES IN SWEEP WATER MODE THROUGH DIFFERENT LIQUID MEMBRANES

Model biogas purification studies were carried out in sweep water mode with different liquid membranes such as pure water, aqueous 30 wt% K_2CO_3 solution and aqueous 20 wt% DEA solution. Pure water was used as sweep liquid for purification of model biogas since CO_2 solubility in water is considerably higher than that of CH_4 or N_2 . Further, it may significantly reduce the cost of pumping the sweep stream. Nonhumidified feed gas was used in all experiments.

Water as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas

The steady state experimental data as well as simulation results using permeator #6 are presented in Table 4-49. Water was introduced through the

Table 4-46

MODEL BIOGAS PURIFICATION STUDIES UNDER VACUUM MODE WITH WATER
AS LIQUID MEMBRANE IN PERMEATOR #6 AND #7 CONNECTED IN SERIES

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Permeate Flow Rate scc/min		Feed Side Pressure psig		Permeate Pressure in of Hg		Feed Outlet Composition Percentage CH ₄ /CO ₂		Permeate Composition Percentage CH ₄ /CO ₂	
	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	Inlet/Outlet	CH ₄ /CO ₂	CH ₄ /CO ₂	CH ₄ /CO ₂	CH ₄ /CO ₂
8	75.0/43.44	0.0/35.17	36.5/32.0	4.1/1.6	89.01/11.48	23.74/77.69						
12	75.0/43.40	0.0/34.08	37.5/32.0	4.2/1.6	88.27/12.19	23.88/77.47						
16	75.0/43.75	0.0/33.70	37.5/32.0	4.2/1.5	88.25/12.06	23.90/77.51						
19	75.0/43.82	0.0/33.30	38.0/32.0	4.3/1.4	88.11/12.37	23.80/77.77 ⁺						
24	75.0/43.72	0.0/33.10	38.0/32.0	4.2/1.3	86.95/13.36	23.91/77.55 ⁺						
Feed flow rate was changed												
30	60.0/33.51	0.0/27.64	37.0/30.0	3.6/0.3	89.35/10.54	26.37/74.27						
32	60.0/33.18	0.0/27.12	38.0/30.0	2.0/0.2	88.45/11.72	27.27/73.83						
41	60.0/32.97	0.0/28.90	38.0/30.0	3.4/1.2	89.86/10.86	27.07/74.69						
45	60.0/33.46	0.0/29.10	38.0/30.0	2.8/1.1	90.76/10.18	26.35/75.51						
49	60.0/32.64	0.0/28.85	39.5/30.0	2.1/1.2	90.70/10.23	27.87/73.96						
51	60.0/33.04	0.0/28.30	40.0/29.0	2.1/1.1	90.33/10.58	28.43/73.27						
60	60.0/33.53	0.0/28.40	39.5/29.0	3.2/1.0	89.57/11.56	27.77/74.96						
67	60.0/32.84	0.0/29.30	39.7/29.0	2.9/1.1	90.01/11.60	27.60/74.93						
71	60.0/33.24	0.0/27.60	40.2/29.0	2.8/1.0	89.46/12.16	28.97/73.46						
73	60.0/32.44	0.0/28.20	40.0/29.0	2.0/1.1	89.15/12.53	28.33/74.22 [*]						
80	60.0/33.62	0.0/27.90	38.2/29.0	3.1/1.0	89.82/11.66	27.15/75.29 [*]						

Feed: 40% CO₂-60% CH₄; Shell Press.: 40 psig; Membrane Liquid: Water; Bath Temp.: 25°C;
After 36 hours shell pressure was raised to 43 psig.

⁺Average CH₄ Recovery: 85.3%; Average CH₄ Recovery : 82.7%

FIGURE 4-34
 CLM STABILITY STUDIES: VACUUM MODE OF OPERATION
 WITH WATER AS MEMBRANE USING
 PERMEATORS #6 AND #7 CONNECTED IN SERIES

Table 4-47

MODEL BIOGAS PURIFICATION STUDIES UNDER VACUUM MODE WITH 7 WT% K_2CO_3 SOLUTION
AS LIQUID MEMBRANE IN PERMEATOR #3

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Permeate Flow Rate scc/min		Feed Side Pressure psig		Permeate Pressure in of Hg		Feed Outlet Composition Percentage		Permeate Composition Percentage	
	Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		N_2/CO_2		N_2/CO_2^*	
1	100/57.1		0/41.7		30.0/27.0		15.5/0.3		95.19/4.14		17.53/81.93	
2	100/58.28				30.0/27.0		16.65/0.3		93.21/6.25			
3	100/58.52		0/40.0		30.0/27.0		18.1/0.3		92.17/7.58		16.54/83.17	
4	100/59.47				30.0/27.0		17.85/0.3		92.13/7.68			
5.5	100/60.12		0/38.96		30.0/27.0		19.15/0.3		90.38/9.63		16.47/83.12	
7	100/60.34				30.0/27.0		18.3/0.15		90.61/10.05			
9	100/61.28		0/37.95		30.0/27.0		18.8/0.15		89.82/10.77		16.68/87.24	
11	100/61.95		0/37.5		30.0/27.0		19.6/0.15		88.36/12.45		16.73/83.92 [*]	

Feed: 40% CO_2 -60% N_2 ; Shell Pressure: 35 psig; Bath Temp.: 25°C; Humidified feed gas;

* N_2 Recovery: 91.23%

Table 4-48

MODEL BIOGAS PURIFICATION STUDIES UNDER VACUUM MODE WITH 7 WT% K_2CO_3 SOLUTION
AS LIQUID MEMBRANE IN PERMEATOR #4

Elapsed Time hrs.	Feed Side Flow Rate scc/min Inlet/Outlet	Permeate Flow Rate scc/min *	Feed Side Pressure psig Inlet/Outlet	Permeate Pressure in of Hg *	Feed Outlet Composition Percentage N_2/CO_2	Permeate Composition Percentage N_2/CO_2
1	100/85.48	15.82	31.0/18.0	0.65	71.57/27.64	29.07/69.52
2	100/87.94	14.52	31.75/18.0	0.65	69.45/29.58	17.96/81.47
4	100/89.67	12.82	30.75/18.0	0.92	68.05/30.71	13.95/84.01
5.5	100/89.16	12.21	31.0/18.0	1.0	67.96/30.83	13.41/84.52
7.5	100/90.73	12.0	31.5/18.0	1.2	66.54/31.47	12.75/84.45
11.5	100/92.0	10.84	31.5/18.0	1.6	65.46/31.59	12.92/83.37
22	100/93.59	**	30.5/18.0	1.1	64.59/34.07	15.3/82.67
24	100/94.82	**	30.75/18.0	1.3	64.78/34.21	16.31/81.73
28	50/44.93	**	31.0/20.7	1.7	69.02/29.78	17.57/80.51
29.5	50/44.90	**	30.5/20.7	2.0	68.25/30.38	17.82/80.43
31	50/44.75	**	30.5/20.7	2.0	68.17/30.96	18.30/80.09

Feed: 40% CO_2 -60% N_2 ; Shell Press: 35 psig; Humidified feed gas;

* Both ends of the permeate side were connected to the vacuum pump.

** Permeate flow at the vacuum pump end was oscillating; Accurate measurement was impossible.

Table 4-49

SIMULATION RESULTS AND STEADY STATE DATA UNDER SWEEP WATER MODE OF OPERATION
WITH MODEL BIOGAS AND WATER AS MEMBRANE IN PERMEATOR #6

Feed Side Flow Rate scc/min in/out	Sweep Water Flow Rate cc/min in	Feed Side Pressure psig in/out	Sweep Water Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Concentration x 10 ⁶ mole/cc N ₂ /CO ₂	Selecti- vity CO ₂ -N ₂
Simulation						
50.0/30.40	115.6	45.0/44.65	15.44/0.0	94.56/5.44	1.0/7.57	42.84
75.0/50.07	126.9	45.85/45.31	16.75/0.0	87.5/12.51	0.91/8.83	42.67
100.0/72.60	111.7	45.63/44.87	14.72/0.0	81.17/18.83	0.92/1.10	43.11
50.0/30.64	95.5	45.0/44.66	24.75/12.0	94.08/5.92	1.04/9.0	43.55
Data						
50.0/32.62	115.6	45.0/43.0	20.0/0.0	90.95/9.62 ¹		
75.0/47.40	126.9	45.85/42.3	21.0/0.0	82.98/17.85 ²		
100.0/74.34	111.7	45.63/43.0	20.0/0.0	82.15/19.27 ³		
50.0/28.0	95.5	45.0/43.5	30.0/12.0	91.47/9.82 ⁴		

Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Water; Shell Press.: 50 psig

¹N₂ Recovery > 99%; ²N₂ Recovery: 87.6%; ³N₂ Recovery > 99%; ⁴N₂ Recovery: 85.1%

larger diameter fibers of permeator #6 to absorb the CO_2 enriched permeate gas as it is expected that pressure drop would be much less compared to the smaller diameter fibers. The sweep water outlet pressure was maintained at one atmosphere for the first three runs. The purification results are highly encouraging.

At 50 sccm feed flow rate, the purified gas streams contain about 10% CO_2 . The N_2 recovery was very high. The pressure drop in the sweep line was not very high. For a sweep flow rate of about 115 cc/min, the pressure drop was approximately 20 psi. The data show that the CO_2 composition in the purified biogas increased with an increase in feed inlet gas flow rate.

In the fourth experiment, sweep water side pressure was raised by using a back pressure regulator to study its effect on separation. The sweep inlet and outlet pressures were maintained at 30 psig and 12 psig, respectively. The feed gas flow rate was kept at 50 sccm. Comparing this set of data with that of first one it is obvious that the magnitude of sweep pressure did not affect the purified gas composition. However, the rate of permeation was slightly higher in this case. Correspondingly, the N_2 recovery was lower. Note that, the flow rate of water is lower in this case. The numerical simulation results are in reasonable agreement with the data.

Purification of model biogas was also carried out in this mode using permeator #8 at two different feed flow rates. The steady state data and simulation results are shown in Table 4-50. Sweep water side pressure was higher compared to permeator #6 because of the smaller fiber diameter.

The higher N_2 recovery in the sweep water mode can be explained in the following way. The mass transfer of a solute in this configuration can be shown schematically in Figure 4-35. Any permeable species has to face three resistances: resistance due to the stationary liquid membrane, the boundary layer resistance in the sweep water side and the gas film resistance from the pore which separates the two liquids. However, for the gas system and the sweep liquid being studied in the present work, the gas phase resistance in the pores is negligible compared to the other two liquid phase resistances. The mass transfer coefficient for each gas species corresponding to the sweep water flow

Table 4-50

SIMULATION RESULTS AND STEADY STATE DATA UNDER SWEEP WATER MODE OF OPERATION
WITH MODEL BIOGAS AND WATER AS MEMBRANE IN PERMEATOR #8

Feed Side Flow Rate scc/min in/out	Sweep Water Flow Rate cc/min in	Feed Side Pressure psig in/out	Sweep Water Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Concentration x 10 ⁶ mole/cc CO ₂ -N ₂	Selecti- vity
Simulation						
50.0/34.53	21.8	45.0/44.73	28.05/0.0	85.55/14.45	1.43/31.22	64.64
35.0/22.16	20.5	45.0/44.82	26.38/0.0	92.64/7.36	1.52/27.42	66.08
Data						
50.0/33.51	21.8	45.0/44.1	29.0/0.0	83.67/16.59 ¹		
35.0/21.70	20.5	45.0/44.1	28.5/0.0	88.73/11.89 ²		
Feed: 40%CO ₂ -60%N ₂ ; Bath Temp.: 25°C; Sweep: Water; Shell Press.: 50 psig ¹ N ₂ Recovery: 93.46%; ² N ₂ Recovery: 96.25%

FIGURE 4-35
CONCENTRATION PROFILE OF ANY PERMEATING SPECIES:
SWEEP WATER MODE OF OPERATION

rate was calculated based on arithmetic concentration difference. The values are presented in Tables 4-51 and 4-52, respectively for permeators #6 and #8.

The overall selectivity was calculated in the following way. Total permeation rate of a species can be written as

$$R_{Ti} = (K_{OL})_i \int_0^{l_t} (\pi D_{FO} N_F S_i P_i^F - \pi D_{SI} N_S C_i^S) dl$$

$$= (K_{OL})_i A_F [\Delta C_{avg}]_i \quad (4-7)$$

$$\text{where } [\Delta C_{avg}]_i = \left[\int_0^{l_t} (\pi D_{FO} N_F S_i P_i^F - \pi D_{SI} N_S C_i^S) dl \right] / A_F$$

$$\text{and } A_F = \pi D_{FO} N_F l_t$$

The selectivity between species i and j is

$$\alpha_{ij} = \frac{[R_T / \Delta C_{avg}]_i S_i}{[R_T / \Delta C_{avg}]_j S_j} \quad (4-8)$$

The k_m values for N_2 were higher than those for CO_2 in all the cases. However, due to lower solubility of N_2 in water, the overall selectivity is higher in the sweep water mode compared to sweep gas mode when water is used as a contained liquid membrane in both modes of operation. Note that the additional resistance in the sweep water side lowers the permeability of both the permeating species.

Water as Liquid Membrane and 40% CO_2 - 60% CH_4 as Feed Gas

A purification run was carried out for an extended period of time using permeators #6 and #7 connected in series. Fresh sweep water was introduced separately into permeators #6 and #7. A regulating valve was provided at the outlet end of one permeator to maintain equal flow rate of water through each permeator. The total sweep water flow rate was 250 cc/min. The experimental results are presented in Table 4-53 and plotted in Figure 4-36. The methane recovery was greater than 95%. However, the CO_2 composition in the purified gas

Table 4-51

MASS TRANSFER COEFFICIENT IN THE SWEEP WATER SIDE
IN PERMEATOR #6

Flow rate cc/min	Velo- city cm/sec	Re		N_{Gz}		N_{Sh}		$k_m \times 10^{-3}$ cm/sec		$K_{OL} \times 10^{-4}$ cm/sec	
		N_2	CO_2	N_2	CO_2	N_2	CO_2	N_2	CO_2	N_2	CO_2
95.5	22.70	60.02	5.61	8.77	2.85	3.50	3.565	2.797	7.54	5.57	
111.7	26.55	70.20	6.57	10.26	3.09	3.70	3.863	2.960	7.81	5.68	
115.6	27.48	72.65	6.80	10.62	3.14	3.74	3.926	2.996	7.88	5.72	
126.9	30.16	79.75	7.46	11.66	3.27	3.86	4.093	3.092	7.70	5.64	

Table 4-52

MASS TRANSFER COEFFICIENT IN THE SWEEP WATER SIDE
IN PERMEATOR #8

Flow rate cc/min	Velo- city cm/sec	N _{Re}		N _{Gz}		N _{Sh}		k _m X 10 ⁻³ cm/sec		K _{OL} X 10 ⁻⁴ cm/sec	
		N ₂	CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂	CO ₂	N ₂	CO ₂
21.8	15.42	16.99	0.935	1.46	0.595	0.929	1.784	1.786	5.18	5.69	
20.5	14.50	15.97	0.880	1.37	0.560	0.874	1.678	1.679	4.97	5.58	

Table 4-53

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP WATER MODE AND WATER AS MEMBRANE
IN PERMEATOR #6 AND #7 CONNECTED IN SERIES

Elapsed time in hr.	Feed Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Inlet Sweep Water Pressure psig in Permeators #6 #7	Feed outlet composition percentage CH ₄ /CO ₂
4	75.0/50.12	45.5/42.5	36.8 36.0	84.18/14.32
8	75.0/49.20	46.0/42.5	37.6 37.0	85.87/13.13
11	75.0/49.33	46.5/41.4	38.0 37.2	86.89/12.12
16	75.0/50.11	46.2/37.0	38.0 37.5	86.25/13.02
20	75.0/51.58	45.3/37.5	37.5 37.0	83.47/15.86
24	75.0/51.69	45.0/37.5	37.5 37.0	83.71/15.43
28	75.0/50.78	45.5/38.0	37.0 36.0	83.98/15.30
33	75.0/51.24	44.75/38.0	36.5 36.0	83.44/16.02
37	75.0/50.03	46.5/38.0	36.0 35.0	84.97/14.30
41	75.0/49.62	47.0/38.0	36.0 35.0	85.64/13.64
43	75.0/50.98	46.25/36.3	36.0 35.0	85.11/14.54

Feed: 40%CO₂-60%CH₄; Bath Temp.: 25°C; Sweep: Water; Shell Press.: 50 psig;
Average sweep water flow rate through permeator #6: 123.85 cc/min;
Average sweep water flow rate through permeator #7: 126.13 cc/min;
Average CH₄ recovery: 95%

Table 4-53 (cont.)

Elapsed time in hr.	Feed Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Inlet Sweep Water Pressure psig in Permeators #6 #7	Feed outlet composition percentage CH ₄ /CO ₂
44	50.0/31.0	45.5/37.5	35.3 34.8	85.32/14.02 ⁺
48	50.0/33.10	47.0/37.5	35.0 34.5	90.28/8.48
52	50.0/31.30	46.5/36.8	34.6 34.0	89.53/8.77
56	50.0/30.20	46.5/36.5	34.5 34.0	90.25/8.27
60	50.0/30.58	45.0/37.0	35.0 34.5	89.29/9.32
62	50.0/30.14	46.2/37.0	35.5 35.0	89.17/9.36
66	50.0/29.80	47.0/36.0	35.5 35.0	90.37/8.34
70	50.0/29.28	45.0/35.5	35.5 35.0	89.83/8.55
74	50.0/30.03	46.0/36.0	35.5 35.0	89.16/9.06
78	50.0/30.52	44.5/36.0	35.5 35.0	89.27/9.25
81	50.0/30.92	44.0/35.5	35.5 35.0	88.89/9.63
84	50.0/30.93	44.5/35.5	35.6 34.4	88.79/9.79
88	50.0/30.95	45.0/37.0	35.0 34.6	88.41/10.14
90	50.0/30.89	45.0/37.0	35.0 34.6	89.51/10.0

Feed: 40%CO₂-60%CH₄; Bath Temp.: 25°C; Sweep: Water; Shell Press.: 50 psig;
⁺Total sweep water flow rate: 199 cc/min;
Average CH₄ recovery: 91%

FIGURE 4-36
 CLM STABILITY STUDIES: SWEEP WATER MODE OF OPERATION
 WITH WATER AS MEMBRANE USING
 PERMEATORS #6 AND #7 CONNECTED IN SERIES

stream was relatively high.

After 43 hours of steady run, the feed gas flow rate was reduced, keeping the feed gas inlet pressure constant. This led to a lower CO_2 composition at the feed gas outlet (about 10%). The average methane recovery was 91%.

30 wt% K_2CO_3 Solution as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas

Model biogas purification run with sweep water and 30 wt% K_2CO_3 solution as membrane was carried out in permeator #6. This run was continued for about 50 hours. The results are shown in Table 4-54. The major difference from all the experiments carried out so far with 30 wt% K_2CO_3 solution was that the feed gas in this case was completely dry. The run was carried out without any stability problem. However, the quality of the purified gas is lower in the present case compared to pure water membrane experiments which can be attributed to the lower permeability of gases through the 30 wt% K_2CO_3 solution and to a much lower water flow rate. Average nitrogen recovery was about 95%.

30 wt% K_2CO_3 Solution as Liquid Membrane and 40% CO_2 - 60% CH_4 as Feed Gas

In this study, permeators #6 and #7 were operated in series. Sweep water was introduced separately through permeators #6 and #7. As in the previous case, the feed gas was introduced without any humidification.

The results are presented in Table 4-55 and plotted in Figure 4-37. The CO_2 composition in the purified feed gas varied between 14 to 16%. The methane recovery was around 93%. The above set of experiments strongly suggest that a trouble-free operation with sweep water mode of operation is obviously feasible. Further high methane recovery is easily achieved.

20 wt% DEA Solution as Liquid Membrane and 40% CO_2 - 60% N_2 as Feed Gas

A long-term experiment using 20 wt% DEA solution as a contained liquid membrane was carried out in permeator #8. Experimental data are reported in Table 4-56. The operation was very stable even though the feed gas mixture was totally dry. For a feed gas flow rate of 50 sccm and sweep water flow rate of 25 cc/min,

Table 4-54

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP WATER MODE AND
30 WT% K₂CO₃ SOLUTION AS MEMBRANE IN PERMEATOR #6

Elapsed time in hr.	Feed Side Flow Rate scc/min inlet/outlet	Sweep Water Flow Rate cc/min	Feed Side Pressure psig inlet/outlet	Sweep Water Pressure psig inlet/outlet	Feed outlet composition percentage N ₂ /CO ₂
2	50.0/32.62	61.86	45.25/44.4	28.0/8.0	85.29/17.65
5	50.0/32.25	82.87	45.25/44.4	32.0/8.0	87.99/14.60
8	50.0/32.77	80.91	45.25/44.4	32.0/8.0	87.84/14.92
11.5	50.0/32.80	80.58	45.25/44.4	32.0/8.0	87.69/15.22
17.5	50.0/33.22	80.71	45.25/44.4	32.0/8.0	86.79/16.09
22	50.0/33.22	78.00	45.30/44.4	32.0/8.0	86.72/16.18
24	50.0/33.22	76.81	45.5/44.4	32.0/8.0	86.38/16.60
26	50.0/33.16	79.36	45.5/44.4	32.0/8.0	86.07/16.78
30	50.0/32.60	78.99	45.5/44.4	32.0/8.0	86.32/16.08
33	50.0/33.08	78.62	45.5/44.4	32.0/8.0	86.20/16.33
36	50.0/32.65	79.30	45.5/44.4	32.0/8.0	86.66/15.96
45.5	50.0/32.89	76.80	45.6/44.4	32.0/8.0	86.18/16.04
51.5	50.0/32.99	79.24	45.5/44.4	32.0/8.0	86.14/16.06

Feed: 40%CO₂-60%N₂; Shell Press.: 50 psig; Membrane Liquid: 30 wt% K₂CO₃ solution;
Bath Temp.: 25°C; Non-humidified feed gas; Sweep: Water;
Average N₂ recovery: 94.7%

Table 4-55

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP WATER MODE AND 30 WT% K_2CO_3 SOLUTION
AS MEMBRANE IN PERMEATOR #6 AND #7 CONNECTED IN SERIES²

Elapsed time in hr.	Feed Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Inlet Sweep Water Pressure psig in Permeators #6 #7	Feed outlet composition percentage CH_4/CO_2
2	50.0/32.44	45.5/43.5	34.5 19.5	82.42/15.2
6	50.0/32.49	46.2/43.5	35.5 19.5	87.53/10.54
10	50.0/33.75	47.5/43.5	34.5 19.5	85.59/12.85
14	50.0/33.08	47.6/44.0	35.7 19.5	85.45/13.42
18	50.0/33.50	48.5/44.0	36.0 19.5	84.58/14.42
22	50.0/34.73	48.2/44.0	36.0 19.7	82.73/16.44
26	50.0/33.13	47.7/44.0	36.0 19.5	84.88/13.67
30	50.0/32.59	47.7/44.0	38.0 20.0	85.04/13.56
34	50.0/32.10	48.3/44.0	37.0 21.0	84.48/13.85
38	50.0/33.08	48.0/44.0	36.5 20.5	84.38/14.15
44	50.0/34.30	48.0/44.0	38.0 21.0	83.02/16.07
48	50.0/34.20	48.5/44.0	38.0 21.5	82.64/16.22

Feed: 40% CO_2 -60% CH_4 ; Shell Press.: 50 psig; Membrane Liquid: 30 wt% K_2CO_3 solution;
Bath Temp.: 25°C; Non-humidified feed gas; Sweep: Water; Average sweep water flow
rates through permeators #6 and #7 were 124.5 cc/min and 129.6 cc/min, respectively;
Average CH_4 recovery: 93.5%

Table 4-55 (contd.)

Elapsed time in hr.	Feed Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Inlet Sweep Water Pressure psig in Permeators #6	Inlet Sweep Water Pressure psig #7	Feed outlet composition percentage CH ₄ /CO ₂
50 ++	50.0/33.78	48.2/44.0	40.5	20.5	82.98/15.79
60	50.0/33.14	46.0/42.0	38.0	21.0	81.28/16.63
63	50.0/33.57	46.2/41.8	41.0	19.0	82.71/15.27
67	50.0/33.58	46.5/41.8	42.0	19.0	82.76/15.35
70	50.0/32.85	46.3/41.8	40.0	21.0	83.32/14.96
73	50.0/33.25	47.0/42.0	40.0	20.0	83.03/15.32
77	50.0/32.86	47.6/42.0	41.0	22.0	82.43/15.99
79	50.0/34.07	48.0/42.0	42.0	21.5	82.25/16.36
83	50.0/33.95	48.7/42.0	42.0	22.0	81.09/17.26
87	50.0/34.29	48.5/42.0	44.5	20.0	81.32/16.78
91	50.0/33.87	48.0/41.7	42.0	22.0	80.73/17.43
95	50.0/33.62	47.5/41.7	44.0	22.0	81.98/16.56
99	50.0/34.24	47.5/41.7	41.0	26.0	81.10/16.98
101	50.0/33.94	47.8/41.7	44.0	24.0	80.93/17.48

Feed: 40%CO₂-60%CH₄; Shell Press.: 50 psig; Membrane Liquid: 30 wt% K₂CO₃ solution;
 Bath Temp.: 25°C; Non-humidified feed gas; Sweep: Water; Average sweep water flow
 rates through permeators #6 and #7 were 124.5 cc/min and 129.6 cc/min, respectively;
 Average CH₄ recovery: 91.94%; ++ Power failure occurred at 51st hour and the run
 restarted at 55th hour.

FIGURE 4-37
CLM STABILITY STUDIES: SWEEP WATER MODE OF OPERATION
WITH 30 WT% K₂CO₃ SOLUTION AS MEMBRANE USING
PERMEATORS #6 AND #7 CONNECTED IN SERIES

Table 4-56

PURIFICATION RUN WITH MODEL BIOGAS IN SWEEP WATER MODE AND
20 WT% DEA SOLUTION AS MEMBRANE IN PERMEATOR #8

Elapsed time in hr.	Feed Side Flow Rate scc/min inlet/outlet	Sweep Water Flow Rate cc/min	Feed Side Pressure psig inlet/outlet	Sweep Water Pressure psig inlet/outlet	Feed outlet composition percent. ge N ₂ /CO ₂
3.5	50.0/33.97	26.47	44.75/44.3	33.0/0.0	85.71/14.14
6.5	50.0/34.89	23.98	44.75/44.3	33.0/0.0	84.49/15.14
19	50.0/35.10	23.29	44.75/44.3	32.8/0.0	83.49/17.07
22	50.0/35.21	25.23	45.00/44.3	32.6/0.0	83.37/16.66
24	50.0/35.69	25.42	45.00/44.3	32.2/0.0	83.34/16.66
27	50.0/35.66	25.48	45.00/44.3	32.0/0.0	82.97/17.03
43	50.0/35.13	21.92	45.25/44.5	30.0/0.0	83.23/17.10
46.5	50.0/35.62	21.09	45.00/44.4	30.0/0.0	82.86/17.27
48	50.0/36.07	21.56	45.0/44.4	30.0/0.0	82.82/17.47
Sweep water flow rate was changed					
49.5	50.0/34.19	35.86	45.25/44.4	48.2/0.0	83.34/16.97
52.5	50.0/33.98	35.82	45.25/44.5	49.0/0.0	86.72/13.46
55	50.0/34.49	35.33	45.25/44.5	49.0/0.0	86.63/13.41
67	50.0/33.97	33.09	45.25/44.5	46.0/0.0	87.29/13.15
71	50.0/33.94	33.00	45.00/44.5	48.6/0.0	86.65/13.71
75.5	50.0/34.47	33.55	45.00/44.5	48.2/0.0	86.56/13.53
79.5	50.0/34.47	33.55	45.00/44.5	48.0/0.0	86.08/13.84

Feed: 40%CO₂-60%N₂; Shell Press.: 50 psig; Membrane Liquid: 20 wt% DEA; Bath Temp.: 25°C;
Non-humidified feed gas; Sweep: Water;
Average N₂ recovery: 98%

Table 4-56 (contd.)

Elapsed time in hr.	Feed Side Flow Rate scc/min inlet/outlet	Sweep Water Flow Rate cc/min	Feed Side Pressure psig inlet/outlet	Sweep Water Pressure psig inlet/outlet	Feed outlet composition percentage N ₂ /CO ₂
91	50.0/33.97	32.36	45.0/44.5	47.2/0.0	86.38/13.76
93.5	50.0/34.43	31.96	45.0/44.5	47.2/0.0	85.90/14.17
95.5	50.0/34.94	32.12	45.0/44.5	47.0/0.0	86.13/13.86
98	50.0/34.95	30.69	45.0/44.5	46.0/0.0	85.94/13.86
Feed gas and sweep water flow rates were changed					
100.5	40.0/26.38	33.99	45.0/44.7	49.5/0.0	87.68/11.92
118	40.0/25.51	32.64	45.0/44.7	47.0/0.0	90.21/9.59
126.5	40.0/25.52	34.92	45.0/44.7	48.0/0.0	90.25/9.51
147	40.0/25.52	33.02	45.0/44.7	45.0/0.0	90.09/9.58
149	40.0/25.02	33.86	45.0/44.7	49.0/0.0	89.97/9.72
163	40.0/25.51	32.22	45.0/44.7	47.5/0.0	90.81/9.22
167.5	40.0/25.53	32.64	45.0/44.6	50.0/0.0	90.69/9.14
172.5	40.0/26.03	32.89	45.0/44.6	51.8/0.0	90.44/9.21
187	40.0/25.52	30.85	45.0/44.6	49.0/0.0	91.26/8.84
191.5	40.0/25.99	32.60	45.0/44.6	49.0/0.0	90.63/9.34
195	40.0/25.99	28.19	45.0/44.6	48.8/0.0	90.55/9.40
211.5	40.0/25.96	29.34	45.0/44.6	48.0/0.0	91.00/9.35
213.5	40.0/25.97	28.34	45.0/44.6	48.5/0.0	90.60/9.53
216	40.0/25.98	29.00	45.0/44.6	48.5/0.0	90.66/9.39

Feed: 40%CO₂-60%N₂; Shell Press.: 50 psig; Membrane Liquid: 20 wt% DEA; Bath Temp.: 25°C;
 Non-humidified feed gas; Sweep: Water;
 Average N₂ recovery: 98%

feed outlet composition stabilized at around 17% CO₂. After 48 hours of operation, the sweep water flow rate was increased. A better performance was obtained at higher water flow rate. The CO₂ composition dropped to around 13-14%. After another 50 hours of stable operation, the feed flow rate was lowered to a value of 40 sccm. The CO₂ composition in the feed outlet dropped to around 9%. The performance was remarkably stable throughout the rest of the experiment. Nitrogen recovery was around 98%. This shows the robust and trouble-free operation with DEA as liquid membrane in sweep water mode is possible with high recovery and reasonably high purity with only a 17-inch-long permeator. Note that the sweep water flow rates used were 1/2 to 1/3 of the sweep water flow rates used with permeators #6 and #7.

ESTIMATION OF EFFECTIVE MEMBRANE THICKNESS IN LARGE PERMEATORS

The experimental procedure for determination of the effective membrane thickness in a large permeator was similar to that for a small permeator. Pure gas permeation studies under conventional mode of operation with water as a liquid membrane have been carried out in all large permeators. The permeated gas was allowed to flow countercurrent to the feed gas stream and it exited the permeator essentially at atmospheric pressure. The permeate flow rate was measured accurately by a bubble flow meter. The governing differential equations for pure gas permeation were then solved for different values of effective membrane thickness. The correct value should match the gas permeation rate obtained experimentally. The pure CO₂ permeation data for large permeators #10, #11 and #12 at different feed flow rates are compared with the simulation results in Tables 4-57, 4-58 and 4-59, and the effective membrane thicknesses are estimated to be in the range of 0.085 inch, 0.0125 inch and 0.011 inch, respectively.

Permeator #10 was the first large-scale permeator fabricated. A totally new fiber matting and bundle preparation procedure was adopted as the number of fibers were very large. In this permeator the feed and the sweep fibers did not mix properly during the bundle preparation procedure as the cotton threads were inserted in between the two fiber layers after the mat was prepared (see Section 3). This caused the two layers of fibers to stay more or less as two separate bunches which resulted in a higher membrane thickness. However, this

Table 4-57

PURE COMPONENT PERMEATION SIMULATION WITH VARIOUS VALUES OF MEMBRANE THICKNESS
AND COMPARISON WITH EXPERIMENTAL DATA IN PERMEATOR #10

	Membrane Thickness inch X 10 ³	Feed Side Flow Rate scc/min inlet/outlet	Permeate Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Permeate Side Pressure psig inlet/outlet
Data		300.0/267.0	0.0/30.10	10.0/9.0	0.15/0.0
Simulation	85.0	300.0/268.12	0.0/31.88	10.0/9.48	0.048/0.0
	87.5	300.0/269.03	0.0/30.97	10.0/9.48	0.046/0.0
	90.0	300.0/269.88	0.0/30.12	10.0/9.48	0.045/0.0
	91.0	300.0/270.21	0.0/29.79	10.0/9.48	0.045/0.0
Data		200.0/165.0	0.0/32.09	10.0/9.9	0.40/0.0
Simulation	85.0	200.0/167.82	0.0/32.18	10.0/9.67	0.048/0.0
	85.25	200.0/167.91	0.0/32.09	10.0/9.67	0.048/0.0
	85.5	200.0/168.01	0.0/31.99	10.0/9.67	0.048/0.0
	86.0	200.0/168.19	0.0/31.81	10.0/9.67	0.048/0.0
Data		150.0/117.40	0.0/33.44	10.0/9.95	0.55/0.0
Simulation	82.0	150.0/116.49	0.0/33.51	10.0/9.76	0.050/0.0
	82.25	150.0/116.59	0.0/33.41	10.0/9.76	0.050/0.0
	83.0	150.0/116.89	0.0/33.11	10.0/9.76	0.049/0.0
	85.0	150.0/117.67	0.0/32.33	10.0/9.76	0.049/0.0

Feed: 99.99% CO₂; Shell Press.: 12 psig; Bath Temp.: 25°C; Membrane Liquid: Water

$$Q_{\text{CO}_2} = 210.0 \times 10^{-9} \text{ (scc-cm/cm}^2\text{-s-cm Hg)}$$

Table 4-58

PURE COMPONENT PERMEATION SIMULATION WITH VARIOUS VALUES OF MEMBRANE THICKNESS
AND COMPARISON WITH EXPERIMENTAL DATA IN PERMEATOR #11

	Membrane Thickness inch X 10 ³	Feed Side Flow Rate scc/min inlet/outlet	Permeate Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Permeate Side Pressure psig inlet/outlet
Data		350.0/158.10	0.0/188.66	10.1/10.0	0.90/0.35
Simulation	12.0	350.0/145.51	0.0/204.49	10.1/9.68	0.63/0.35
	12.5	350.0/153.59	0.0/196.41	10.1/9.67	0.62/0.35
	13.0	350.0/161.05	0.0/188.95	10.1/9.67	0.61/0.35
	13.5	350.0/167.97	0.0/182.03	10.1/9.66	0.60/0.35
Data		400.0/186.52	0.0/204.74	10.2/10.1	0.90/0.35
Simulation	11.5	400.0/185.42	0.0/214.58	10.2/9.71	0.64/0.35
	12.0	400.0/194.24	0.0/205.76	10.2/9.70	0.63/0.35
	12.5	400.0/202.37	0.0/197.63	10.2/9.70	0.62/0.35
Data		500.0/300.80	0.0/193.42	10.0/9.7	0.90/0.35
Simulation	12.0	500.0/300.47	0.0/199.53	10.0/9.31	0.62/0.35
	12.38	500.0/306.45	0.0/193.55	10.0/9.31	0.61/0.35
	13.0	500.0/315.64	0.0/184.36	10.0/9.30	0.60/0.35

Feed: 99.99% CO₂; Shell Press.: 12 psig; Bath Temp.: 25°C; Membrane Liquid: Water

$$Q_{\text{CO}_2} = 210.0 \times 10^{-9} \text{ (scc-cm/cm}^2\text{-s-cm Hg)}$$

Table 4-59

PURE COMPONENT PERMEATION SIMULATION WITH VARIOUS VALUES OF MEMBRANE THICKNESS
AND COMPARISON WITH EXPERIMENTAL DATA IN PERMEATOR #12

	Membrane Thickness inch X 10 ³	Feed Side Flow Rate scc/min inlet/outlet	Permeate Side Flow Rate scc/min inlet/outlet	Feed Side Pressure psig inlet/outlet	Permeate Side Pressure psig inlet/outlet
Data		350.0/119.7	0.0/228.7	10.5/10.0	0.68/0.05
Simulation	11.0	350.0/110.71	0.0/239.29	10.5/10.12	0.38/0.05
	11.5	350.0/120.96	0.0/229.04	10.5/10.11	0.37/0.05
	12.0	350.0/130.38	0.0/219.62	10.5/10.1	0.36/0.05
Data		400.0/152.75	0.0/234.73	10.2/9.8	0.65/0.00
Simulation	10.0	400.0/146.09	0.0/253.01	10.2/9.74	0.40/0.05
	10.75	400.0/163.54	0.0/236.46	10.2/9.73	0.38/0.05
	12.0	400.0/187.84	0.0/212.16	10.2/9.70	0.34/0.05

Feed: 99.99% CO₂; Shell Press.: 12 psig; Bath Temp.: 25°C; Membrane Liquid: Water

$$Q_{\text{CO}_2} = 210.0 \times 10^{-9} \text{ (scc-cm/cm}^2 \text{-s-cm Hg)}$$

problem was eliminated in the making of the large permeators #11 and #12.

A similar gas permeation experiment was also carried out in Permeator #11 with N_2 as a feed gas. The steady state experimental data and the simulation results are shown in Table 4-60. This experiment indicated a liquid membrane thickness of 0.006 inch which was much lower than that obtained with pure CO_2 permeation studies. Steady state separation runs with CO_2 - N_2 gas mixture, described later, were carried out in order to explain this anomalous behavior.

PURIFICATION STUDIES OF MODEL BIOGAS MIXTURES IN LARGE SCALE OPERATION

Model biogas purification studies in large-scale operation were carried out with Permeators #11 and #12 only under sweep gas mode of operation. Pure water and aqueous solution of 20 wt% DEA were utilized as liquid membranes. For pure water membrane, the gas streams were not humidified. For long-term experiment, the feed gas mixture was created by blending commercial grade CO_2 and N_2 (or CH_4) gases. The actual gas composition was determined at the end of the experiment by injecting the feed mixture into the gas chromatograph column. All experiments were carried out at 25°C. Pure helium gas was used to pressurize the shell liquid storage tank. For CO_2 - N_2 feed gas mixture, helium was used as a sweep gas whereas N_2 sweep gas was used for CO_2 - CH_4 feed gas mixture.

Water as Liquid Membrane and CO_2 - N_2 Gas Mixture as Feed

Two different values of membrane thickness were obtained for permeator #11. These two different values were determined from pure CO_2 and pure N_2 permeation studies through pure water as a liquid membrane. A hollow-fiber-contained liquid membrane permeator has four potted ends. Any one of them can be used to introduce the feed gas. For pure N_2 permeation run, the feed nitrogen was introduced through the potted end #2. The same end was not utilized for pure CO_2 permeation studies. It was anticipated that there was some contamination of the feed gas into the sweep gas when a particular potted end was used as the feed inlet end. In order to resolve the problem and to identify the potted end, four steady state purification runs were carried out under identical conditions. In each case, the feed inlet end was changed. The feed and sweep gas flow rates were maintained at 750 and 1000 sccm, respectively. In all runs

Table 4-60

PURE COMPONENT PERMEATION SIMULATION WITH VARIOUS VALUES OF MEMBRANE THICKNESS
AND COMPARISON WITH EXPERIMENTAL DATA IN PERMEATOR #11

	Membrane Thickness inch x 10 ³	Feed Side		Permeate Side		Feed Side		Permeate Side	
		Flow Rate scc/min	inlet/outlet	Flow Rate scc/min	inlet/outlet	Pressure psig	inlet/outlet	Pressure psig	inlet/outlet
Data		300.0/262.72		0.0/32.13		30.5/30.5		0.50/0.05	
Simulation	6.0	300.0/264.75		0.0/35.25		30.5/30.2		0.11/0.05	
	6.50	300.0/267.46		0.0/32.54		30.5/30.2		0.11/0.05	
	6.75	300.0/269.78		0.0/30.22		30.5/30.2		0.10/0.05	

Feed: 99.99% N₂; Shell Press.: 35 psig; Bath Temp.: 25°C; Membrane Liquid: Water

$$Q_{N_2} = 5.58 \times 10^{-9} \text{ (scc-cm/cm}^2\text{-s-cm Hg)}$$

dry feed gas was introduced into the permeator at an inlet pressure of 45 psig. The sweep helium gas was introduced countercurrent to the feed gas mixture and the liquid membrane pressure was kept at 50 psig.

The steady state results of the separation runs are presented in Table 4-61. The permeation rates in the first two cases are considerably higher than the other two suggesting some kind of contamination. The nitrogen recovery value is also considerably low. Note that, for the first two data sets the feed gas was introduced through the bent fiber set. It was clear that high-pressure feed gas could not be used in the bent fiber set. In subsequent experiments, the feed was therefore introduced through the straight fiber set.

To determine the stability of a large-scale hollow-fiber-contained liquid membrane system, separation studies were carried out over a period of 245 hrs. (10 days) using 41% CO₂ - 58% N₂ (1% impurities) model biogas mixture as feed in permeator #11. As Table 4-62 indicates, the flow rates and pressures of various streams were stable. The performance was essentially steady with an average N₂ recovery of ~87%. The CO₂ composition in the purified gas stream was in the range of 12 to 14%. The pressure drop in the feed stream was negligible and that of the sweep stream was only about 5 psi for the flow rates used in this study. The compositions of the feed and sweep outlet streams for the entire period are shown in Figure 4-38.

The results demonstrate that long-term separation of CO₂ can be carried out efficiently and stably in a large-scale hollow-fiber-contained liquid membrane permeator with pure water as a liquid membrane without any operational difficulty.

20 wt% DEA Solution as Liquid Membrane and CO₂ - N₂ Gas Mixture as Feed

One month-long life test of a hollow-fiber-contained liquid membrane permeator system was made with a feed mixture containing 41% CO₂ and 58% N₂. Two large permeators (#11 and #12) were connected in series for this study i.e., the purified gas stream from the first permeator was introduced as the feed in the second permeator. However, no such series connection was made in the sweep line. Pure helium sweep gas was introduced in each permeator. (The connections

Table 4-61

PURIFICATION RUNS UNDER SWEEP GAS MODE OF OPERATION WITH MODEL BIOGAS
AND WATER AS MEMBRANE IN LARGE SCALE PERMEATOR #11

Feed Side Flow Rate scc/min in/out	Sweep Side Flow Rate scc/min in/out	Feed Side Pressure psig in/out	Sweep Side Pressure psig in/out	Feed Outlet Composition Percentage N ₂ /CO ₂ *	Sweep Outlet Composition Percentage N ₂ /CO ₂ *	Nitrogen Recovery Percentage
750.0/378.51	1000.0/1436.39	45.5/45.3	7.2/1.5	71.20/21.91	10.81/14.11	60 ¹
750.0/446.15	1000.0/1370.76	45.5/45.4	7.0/1.4	73.27/20.17	6.79/14.06	73 ²
750.0/498.72	1000.0/1324.88	45.8/45.5	7.0/1.5	74.30/20.07	3.94/13.99	82 ³
750.0/528.20	1000.0/1294.54	45.8/45.2	6.6/1.4	76.02/20.41	2.16/13.84	89 ⁴

* Balance Helium; Feed: 40%CO₂-60%N₂; Bath Temp.: 25°C; Sweep: Helium;

Shell Press.: 50 psig; Membrane Liquid: Water

1 Feed Inlet: End #2; Feed Outlet: End #4; Sweep Inlet: End #3; Sweep Outlet: End #1
 2 Feed Inlet: End #4; Feed Outlet: End #2; Sweep Inlet: End #1; Sweep Outlet: End #3
 3 Feed Inlet: End #3; Feed Outlet: End #1; Sweep Inlet: End #2; Sweep Outlet: End #4
 4 Feed Inlet: End #1; Feed Outlet: End #3; Sweep Inlet: End #4; Sweep Outlet: End #2

Table 4-62

LONG TERM PURIFICATION RUN WITH MODEL BIOGAS FEED MIXTURE IN SWEEP GAS MODE
AND PURE WATER AS A MEMBRANE IN LARGE SCALE PERMEATOR #11

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage	N ₂ /CO ₂ *	Composition Percentage	N ₂ /CO ₂ *
4.5	400.0/243.10	1000.0/1201.40	45.0/45.0	45.0/45.0	6.6/1.3	81.84/12.56	1.54/10.04					
11.0	400.0/245.26	1000.0/1199.97	45.0/45.0	45.0/45.0	6.5/1.5	80.98/14.02	1.54/9.77					
26.0	400.0/247.98	1000.0/1195.96	45.0/45.0	45.0/45.0	6.5/1.3	81.48/14.38	1.49/9.81					
31.0	400.0/247.19	1000.0/1195.69	45.0/45.0	45.0/45.0	6.5/1.3	81.11/14.28	1.51/9.83					
48.0	400.0/247.45	1000.0/1191.16	45.0/45.0	45.0/45.0	6.5/1.3	82.18/14.42	1.47/9.92					
52.0	400.0/250.93	1000.0/1186.03	45.0/45.0	45.0/45.0	6.5/1.3	81.50/14.82	1.39/9.67					
58.0	400.0/249.93	1000.0/1184.66	45.0/45.0	45.0/45.0	6.5/1.4	81.46/14.70	1.41/9.81					
72.0	400.0/243.88	1000.0/1201.21	45.0/45.0	45.0/45.0	6.6/1.4	82.51/14.26	1.38/9.71					
76.0	400.0/245.39	1000.0/1197.33	45.0/45.0	45.0/45.0	6.6/1.4	82.23/14.17	1.38/9.71					
81.5	400.0/248.72	1000.0/1196.10	45.0/45.0	45.0/45.0	6.6/1.4	81.82/14.54	1.41/9.83					

Table 4-62 (cont..)

Elap- sed Time hrs.	Feed Side Flow Rate scc/min		Sweep Side Flow Rate scc/min		Feed Side Pressure psig		Sweep Side Pressure psig		Feed Outlet Composition Percentage N ₂ /CO ₂ *		Sweep Outlet Composition Percentage N ₂ /CO ₂ *	
	Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		N ₂ /CO ₂ *		N ₂ /CO ₂ *	
120.5	400.0/255.85		1000.0/1180.33		45.0/45.0		6.9/1.9		81.55/13.85		1.59/10.21	
144.0	400.0/244.07		1000.0/1204.26		45.0/45.0		6.6/1.4		82.60/12.36		1.52/10.16	
151.5	400.0/240.70		1000.0/1210.03		44.8/44.8		6.6/1.4		82.57/12.20		1.53/9.94	
168.0	400.0/240.86		1000.0/1207.11		44.8/44.8		6.6/1.4		83.08/11.84		1.56/10.25	
172.0	400.0/236.30		1000.0/1210.74		44.8/44.8		6.6/1.4		83.21/11.58		1.50/10.30	
180.0	400.0/242.46		1000.0/1195.37		45.0/45.0		6.6/1.4		82.42/11.88		1.50/10.30	
195.5	400.0/240.12		1000.0/1204.09		45.0/45.0		6.6/1.4		82.76/11.66		1.48/10.19	
200.5	400.0/241.24		1000.0/1202.53		45.0/45.0		6.6/1.4		82.68/11.76		1.52/10.35	
217.5	400.0/240.82		1000.0/1202.79		45.0/45.0		6.6/1.4		83.46/11.68		1.52/10.32	
238.5	400.0/241.52		1000.0/1203.15		45.2/45.0		6.6/1.4		82.64/11.57		1.53/10.28	
245.0	400.0/242.38		1000.0/1203.90		45.2/45.0		6.6/1.4		82.58/11.86		1.43/10.24	

* Balance Helium; Feed: 41%CO₂-58%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Shell liquid pressurized with helium;
Nonhumidified feed and sweep gas; N₂ Recovery: ~87%

FIGURE 4-38

CLM STABILITY STUDIES: SWEEP GAS MODE OF OPERATION

WITH WATER AS A MEMBRANE IN PERMEATOR #11

were made as follows. After measurement of the total sweep inlet flow rate, the stream was divided in two by a tee and was connected to the sweep inlet end of each permeator. Similarly, the sweep outlet streams from two permeators were also joined by another tee before it was sent to the GC for analysis.)

Initially, a feed flow rate of 350 scc/min was maintained at a pressure of 45 psig for about 2 days. The total sweep flow rate was 1200 scc/min. There was virtually no pressure drop in the feed line and the purified gas contained only 3 to 4% of CO_2 . The average N_2 recovery was 79%. This observation led us to believe that the available membrane area in two permeators would be able to process a higher feed flow rate. Therefore, after two days of operation, the feed flow rate was increased to 475 scc/min without altering the total sweep flow rate. The performance for the entire period is shown in Table 4-63. The outlet gas compositions and the N_2 recovery are plotted against the elapsed time in Figure 4-39. An excellent and steady performance was observed. At higher feed flow rate of 475 scc/min, the CO_2 content in the purified gas was generally less than 10% with an average N_2 recovery of 87%. The pressure drop in both streams was very low. To avoid local drying of the membrane liquid over such a long period of time, about 50 ml. of membrane liquid was purged out from each permeator after every 5 days of continuous operation without disturbing the experiment.

The results show that the hollow-fiber-contained liquid membrane system can be used efficiently to separate gas mixtures with minimum maintenance over a prolonged time period. In an actual operation a slow and steady recirculation of the membrane liquid (if the membrane liquid is a solution instead of a pure liquid) would completely eliminate the problem of local drying, if any, within the permeator.

Two more short-term experiments were carried out with CO_2 - N_2 feed mixture and 20 wt% DEA solution as a liquid membrane. Both experiments used Permeators #11 and #12 in series as mentioned earlier. These two experiments were made in response to the enquiries by two companies e.g., Permapure Products, Inc. and Ecolotrol (see section 6). The first experiment utilized a feed gas mixture containing 41% CO_2 and 58% N_2 but the feed inlet pressure was close to atmospheric (problem posed by Ecolotrol). The steady state data is shown in

Table 4-63

LONG TERM PURIFICATION RUN WITH MODEL BIOGAS FEED MIXTURE IN SWEEP GAS MODE AND
20 WT% DEA AS A LIQUID MEMBRANE IN LARGE SCALE PERMEATORS #11 AND #12 IN SERIES

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *
2.0	380.0/176.52		1200.0/1578.46		45.2/45.0		4.5/1.6		88.63/2.50		3.17/10.02	
3.0	380.0/176.37		1200.0/1578.11		45.2/45.0		4.5/1.6		88.42/2.75		3.16/10.05	
4.0	380.0/176.28		1200.0/1578.35		45.2/45.0		4.5/1.6		88.35/2.86		3.14/10.04	
5.0	380.0/177.54		1200.0/1576.78		45.2/45.0		4.5/1.6		88.30/2.89		3.17/10.16	
6.0	380.0/178.56		1200.0/1575.31		45.2/45.0		4.5/1.6		88.42/3.04		3.18/10.28	
7.0	380.0/181.07		1200.0/1574.47		45.2/45.0		4.5/1.6		88.41/3.03		3.20/10.34	
8.0	380.0/183.68		1200.0/1570.28		45.2/45.0		4.5/1.5		88.50/2.89		3.23/10.36	
9.0	380.0/184.86		1200.0/1570.00		45.2/45.0		4.5/1.5		88.97/2.71		3.16/10.09	
11.0	380.0/186.12		1200.0/1569.70		45.2/45.0		4.5/1.5		88.54/4.04		2.95/9.89	
13.0	380.0/187.11		1200.0/1565.76		45.2/45.0		4.5/1.5		87.67/5.82		2.62/9.73	
15.0	380.0/190.92		1200.0/1564.58		45.2/45.0		4.5/1.4		86.77/7.26		2.52/9.56	
17.0	380.0/195.11		1200.0/1558.47		45.2/45.0		4.5/1.4		86.07/8.21		2.47/9.44	
20.0	380.0/204.70		1200.0/1545.51		45.2/45.0		4.4/1.3		85.07/9.86		2.15/9.05	
22.0	380.0/198.83		1200.0/1567.55		45.2/45.0		4.5/1.3		86.89/6.70		2.42/10.66	
24.0	380.0/190.99		1200.0/1579.66		45.2/45.0		4.5/1.3		89.37/3.72		2.34/9.99	
26.0	380.0/190.94		1200.0/1563.15		45.2/45.0		4.5/1.3		89.29/3.81		2.35/10.09	
28.0	380.0/187.48		1200.0/1564.19		45.2/45.0		4.5/1.3		89.23/3.60		2.33/10.01	
31.0	380.0/193.52		1200.0/1557.66		45.2/45.0		4.5/1.4		89.28/3.72		2.36/10.22	
34.0	380.0/191.47		1200.0/1556.78		45.2/45.0		4.5/1.4		89.54/3.06		2.38/10.32	
36.0	380.0/190.40		1200.0/1556.43		45.2/45.0		4.5/1.4		89.54/3.06		2.38/10.32	
39.0	380.0/189.39		1200.0/1557.14		45.2/45.0		4.5/1.5		89.59/2.83		2.38/10.36	
41.0	380.0/188.14		1200.0/1561.18		45.2/45.0		4.5/1.6		89.77/2.75		2.36/10.25	
44.0	380.0/186.69		1200.0/1566.53		45.2/45.0		4.5/1.6		89.72/2.95		2.26/9.84	

Table 4-63 (contd.)

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *
46.0	380.0/190.07		1200.0/1562.22		45.2/45.0	4.5/1.6			89.58/3.33		2.25/9.89	
47.5	380.0/192.32		1200.0/1558.43		45.2/45.0	4.5/1.6			89.40/3.63		2.22/9.90	
50.0	380.0/188.63		1200.0/1563.65		45.2/45.0	4.6/1.6			89.36/3.62		2.18/9.80	
52.0	380.0/189.67		1200.0/1562.33		45.2/45.0	4.6/1.6			89.15/3.91		2.20/9.90 ⁺	
Feed flow rate was changed												
56.0	475.0/265.82		1200.0/1575.71		45.5/45.0	4.5/1.6			88.31/7.13		2.21/12.02	
60.0	475.0/267.89		1200.0/1573.61		45.5/45.0	4.5/1.5			88.58/7.24		2.18/11.89	
64.0	475.0/273.53		1200.0/1566.55		45.5/45.0	4.3/1.4			88.46/7.58		2.15/11.86	
68.0	475.0/276.57		1200.0/1559.32		45.5/45.0	4.3/1.4			88.41/7.98		2.17/12.14	
70.0	475.0/280.36		1200.0/1560.18		45.5/45.0	4.3/1.4			88.91/7.64		2.22/12.37	
74.0	475.0/273.91		1200.0/1562.64		45.5/45.0	4.3/1.3			89.32/6.92		2.19/12.17	
76.0	475.0/274.58		1200.0/1567.96		45.5/45.0	4.3/1.3			88.91/7.46		2.15/12.06	
78.0	475.0/275.45		1200.0/1572.48		45.5/45.0	4.3/1.3			88.68/7.79		2.13/12.01	
80.0	475.0/276.36		1200.0/1577.69		45.5/45.0	4.3/1.3			88.58/8.03		2.10/11.90	
84.0	475.0/277.20		1200.0/1569.34		45.5/45.0	4.2/1.3			88.42/8.34		2.10/11.97	
88.0	475.0/278.31		1200.0/1569.84		45.5/45.0	4.2/1.3			88.25/8.49		2.10/11.92	
92.0	475.0/279.32		1200.0/1554.47		45.5/45.0	4.3/1.4			88.25/8.61		2.07/11.95	
96.0	475.0/272.74		1200.0/1558.86		45.5/45.0	4.2/1.3			88.83/7.90		2.12/12.20	
100.0	475.0/273.52		1200.0/1559.47		45.5/45.0	4.2/1.3			89.10/7.27		2.11/12.16	
104.0	475.0/273.48		1200.0/1561.56		45.5/45.0	4.2/1.3			88.92/7.38		2.08/11.99	
108.0	475.0/272.16		1200.0/1563.04		45.5/45.0	4.2/1.3			88.46/7.68		2.05/11.88	
112.0	475.0/270.83		1200.0/1564.77		45.5/45.0	4.2/1.3			88.11/7.92		2.01/11.75	
116.0	475.0/268.99		1200.0/1568.89		45.5/45.0	4.2/1.3			87.79/8.48		1.95/11.43	
118.0	475.0/271.97		1200.0/1569.19		45.5/45.0	4.2/1.3			87.48/9.04		1.93/11.41	
120.0	475.0/269.76		1200.0/1573.12		45.5/45.0	4.5/1.7			87.54/8.88		1.96/11.39	

+ Average N₂ recovery: 79%

Table 4-63 (contd.)

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *
122.0	475.0/268.59		1200.0/1576.73		45.5/45.0		4.5/1.6		87.72/8.77		1.93/11.42	
124.0	475.0/269.88		1200.0/1580.43		45.5/45.0		4.5/1.6		87.79/8.68		1.93/11.43	
126.0	475.0/269.76		1200.0/1577.53		45.5/45.0		4.2/1.3		87.98/8.67		1.97/11.66	
128.0	475.0/271.53		1200.0/1575.14		45.5/45.0		4.2/1.3		88.49/8.06		2.00/11.84	
132.0	475.0/273.58		1200.0/1572.26		45.5/45.0		4.2/1.3		88.45/8.32		1.99/11.77	
136.0	475.0/274.41		1200.0/1570.33		45.5/45.0		4.3/1.3		88.08/8.74		1.95/11.63	
140.0	475.0/275.03		1200.0/1565.24		45.5/45.0		4.0/1.3		87.87/9.21		1.92/11.43	
142.0	475.0/274.90		1200.0/1566.88		45.5/45.0		4.0/1.3		87.84/9.31		1.93/11.61	
144.0	475.0/272.83		1200.0/1566.88		45.5/45.0		4.0/1.3		87.98/9.02		1.95/11.71	
146.0	475.0/267.32		1200.0/1577.80		45.5/45.0		4.0/1.3		88.32/8.51		1.90/11.34	
150.0	475.0/271.88		1200.0/1569.86		45.5/45.0		4.0/1.3		87.04/10.09		1.83/11.08	
156.0	475.0/271.65		1200.0/1567.81		45.5/45.0		4.0/1.3		87.57/9.20		1.93/11.85	
158.0	475.0/270.67		1200.0/1561.69		45.5/45.0		4.0/1.3		88.68/7.75		1.98/12.03	
160.0	475.0/274.02		1200.0/1560.99		45.5/45.0		4.5/1.5		89.27/6.88		2.00/12.08	
162.0	475.0/273.20		1200.0/1568.46		45.5/45.0		4.5/1.6		89.67/6.42		1.96/11.78	
164.0	475.0/269.80		1200.0/1579.34		45.5/45.0		4.5/1.6		89.08/7.33		1.91/11.53	
166.0	475.0/274.52		1200.0/1563.77		45.5/45.0		4.5/1.6		88.20/8.61		1.87/11.25	
170.0	475.0/277.05		1200.0/1553.78		45.5/45.0		4.5/1.7		87.69/9.54		1.76/10.85	
172.0	475.0/269.64		1200.0/1575.35		45.5/45.0		4.5/1.7		88.66/7.63		1.84/11.58	
174.0	475.0/274.82		1200.0/1559.46		45.5/45.0		4.5/1.7		87.89/8.57		1.85/11.63	
178.0	475.0/278.14		1200.0/1556.87		45.5/45.0		4.5/1.6		87.71/8.85		1.87/11.84	
182.0	475.0/274.03		1200.0/1557.10		45.5/45.0		4.5/1.5		89.27/6.86		1.93/12.12	
186.0	475.0/269.87		1200.0/1559.63		45.5/45.0		4.2/1.3		89.87/6.12		1.95/12.22	
188.0	475.0/262.76		1200.0/1569.77		45.5/45.0		4.2/1.3		90.18/5.82		1.92/12.02	

Table 4-63 (contd.)

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *
190.0	475.0/267.89		1200.0/1566.28		45.5/45.0		4.2/1.3		89.43/6.82		1.79/11.40	
194.0	475.0/271.21		1200.0/1574.19		45.5/45.0		4.5/1.6		87.83/8.59		1.80/11.70	
196.0	475.0/270.45		1200.0/1576.43		45.5/45.0		4.5/1.6		88.17/8.13		1.77/11.52	
200.0	475.0/275.55		1200.0/1562.55		45.5/45.0		4.5/1.6		88.87/7.63		1.83/12.03	
204.0	475.0/270.03		1200.0/1557.25		45.5/45.0		4.5/1.6		89.54/6.95		1.87/12.14	
208.0	475.0/268.99		1200.0/1553.71		45.5/45.0		4.5/1.6		89.93/6.65		1.87/12.12	
212.0	475.0/267.99		1200.0/1571.96		45.5/45.0		4.5/1.7		89.49/7.51		1.78/11.57	
214.0	475.0/272.77		1200.0/1570.38		45.5/45.0		4.5/1.7		88.76/8.68		1.74/11.40	
216.0	475.0/276.53		1200.0/1570.42		45.5/45.0		4.5/1.7		87.84/9.80		1.70/11.42	
220.0	475.0/270.66		1200.0/1580.91		45.5/45.0		4.2/1.3		89.23/8.25		1.77/11.79	
224.0	475.0/276.20		1200.0/1563.96		45.5/45.0		4.2/1.3		89.20/8.59		1.79/11.93	
228.0	475.0/276.49		1200.0/1559.00		45.5/45.0		4.2/1.3		89.45/8.28		1.81/12.02	
232.0	475.0/274.53		1200.0/1558.27		45.5/45.0		4.2/1.3		89.84/7.80		1.82/12.08	
236.0	475.0/278.21		1200.0/1557.32		45.5/45.0		4.2/1.3		90.03/7.68		1.82/12.16	
240.0	475.0/281.69		1200.0/1548.80		45.5/45.0		4.2/1.3		89.03/9.00		1.76/11.93	
244.0	475.0/278.56		1200.0/1537.80		45.5/45.0		4.5/1.7		88.38/9.77		1.75/11.91	
248.0	475.0/280.84		1200.0/1541.76		45.5/45.0		4.5/1.6		88.41/9.84		1.76/11.89	
252.0	475.0/280.84		1200.0/1548.36		45.5/45.0		4.2/1.3		88.54/9.77		1.75/11.98	
256.0	475.0/283.48		1200.0/1536.59		45.5/45.0		4.2/1.3		88.80/9.49		1.75/12.01	
260.0	475.0/282.26		1200.0/1536.78		45.8/45.2		4.2/1.3		89.03/9.39		1.79/12.31	
264.0	475.0/282.97		1200.0/1541.31		45.8/45.2		4.2/1.3		90.95/7.27		1.83/12.55	
268.0	475.0/286.31		1200.0/1537.24		45.8/45.2		4.2/1.3		89.68/8.80		1.76/12.28	
272.0	475.0/290.30		1200.0/1528.73		45.8/45.2		4.6/1.7		89.08/9.59		1.72/12.05	
276.0	475.0/290.30		1200.0/1535.29		45.8/45.2		4.2/1.3		88.16/10.76		1.68/11.83	

Table 4-63 (contd.)

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *
280.0	475.0/289.63		1200.0/1537.28		45.8/45.2		4.2/1.3		87.58/11.45		1.65/11.67	
284.0	475.0/290.95		1200.0/1545.73		45.8/45.2		4.2/1.3		86.39/12.67		1.58/10.97	
286.0	475.0/290.95		1200.0/1556.62		45.8/45.2		4.5/1.7		88.85/9.73		1.67/11.63	
290.0	475.0/285.00		1200.0/1157.61		45.8/45.2		4.3/1.3		87.75/10.55		1.67/11.55	
294.0	475.0/286.63		1200.0/1555.90		45.5/45.2		4.3/1.3		87.15/11.30		1.56/11.09	
298.0	475.0/268.64		1200.0/1563.79		45.5/45.2		4.3/1.3		90.91/7.18		1.71/11.00	
304.0	475.0/269.57		1200.0/1557.43		45.5/45.2		4.3/1.3		90.66/6.70		1.84/12.47	
308.0	475.0/268.68		1200.0/1578.37		45.5/45.2		4.3/1.3		90.22/7.49		1.67/11.40	
314.0	475.0/280.23		1200.0/1562.10		45.5/45.2		4.3/1.3		88.62/9.36		1.65/11.50	
318.0	475.0/276.68		1200.0/1574.27		45.5/45.2		4.3/1.3		89.31/8.23		1.73/12.05	
320.0	475.0/276.73		1200.0/1563.98		45.5/45.2		4.3/1.3		90.24/6.98		1.79/12.25	
324.0	475.0/280.54		1200.0/1561.96		45.5/45.2		4.3/1.3		88.84/9.06		1.68/11.82	
334.0	475.0/277.84		1200.0/1569.10		45.5/45.2		4.3/1.3		90.71/6.82		1.78/12.15	
336.0	475.0/276.88		1200.0/1569.72		45.5/45.2		4.3/1.3		89.99/7.77		1.68/11.19	
344.0	475.0/281.49		1200.0/1556.84		45.5/45.0		4.3/1.3		88.82/8.48		1.74/12.24	
348.0	475.0/281.40		1200.0/1551.84		45.5/45.0		4.3/1.3		89.94/7.25		1.75/12.34	
356.0	475.0/278.23		1200.0/1560.16		45.5/45.0		4.8/1.8		89.75/7.80		1.65/11.67	
360.0	475.0/283.06		1200.0/1552.49		45.5/45.0		4.8/1.8		88.60/9.11		1.62/11.68	
368.0	475.0/288.31		1200.0/1545.55		45.5/45.0		4.8/1.8		87.77/9.26		1.64/11.94	
380.0	475.0/280.84		1200.0/1561.72		45.5/45.0		4.8/1.8		87.85/9.36		1.56/11.25	
384.0	475.0/283.90		1200.0/1561.18		45.5/45.0		4.8/1.8		87.05/10.09		1.55/11.30	
390.0	475.0/285.76		1200.0/1560.78		45.5/45.0		4.8/1.8		88.29/8.35		1.64/11.95	
402.0	475.0/280.89		1200.0/1557.03		45.5/45.0		5.0/2.1		90.73/5.68		1.72/12.23	
414.0	475.0/293.75		1200.0/1537.34		45.5/45.0		4.7/1.3		88.82/8.38		1.65/12.33	
430.0	475.0/290.45		1200.0/1566.72		45.5/45.0		4.4/1.3		90.30/6.74		1.64/12.09	
438.0	475.0/283.31		1200.0/1613.62		45.5/45.0		5.0/1.5		90.33/6.63		1.70/11.96	
454.0	475.0/301.63		1200.0/1548.85		45.2/45.0		5.0/2.0		86.38/12.69		0.82/11.07	
458.0	475.0/300.25		1200.0/1554.09		45.3/45.0		5.0/2.0		87.25/11.67		0.84/11.27	

Table 4-63 (contd.)

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Sweep Side Flow Rate scc/min		Feed Side Pressure psig		Sweep Side Pressure psig		Feed Outlet Composition Percentage N ₂ /CO ₂ *		Sweep Outlet Composition Percentage N ₂ /CO ₂ *	
	Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		N ₂ /CO ₂ *		N ₂ /CO ₂ *	
482.0	475.0/289.61		1200.0/1598.42		45.3/45.0		4.5/1.8		89.20/9.22		0.89/11.39	
490.0	475.0/291.35		1200.0/1566.57		45.4/45.0		4.6/1.5		89.31/8.84		0.93/11.80	
502.0	475.0/292.52		1200.0/1570.57		45.5/45.0		4.6/1.5		89.23/8.91		0.88/11.48	
508.0	475.0/294.25		1200.0/1572.14		45.5/45.0		5.0/2.0		88.63/9.60		0.85/11.36	
516.0	475.0/294.42		1200.0/1534.15		45.5/45.0		5.0/2.0		89.53/8.35		0.91/11.86	
528.0	475.0/296.60		1200.0/1534.15		45.5/45.0		5.0/2.0		89.12/9.39		0.81/11.02	
532.0	475.0/295.20		1200.0/1542.70		45.5/45.0		4.5/1.4		88.45/9.84		0.84/11.59	
538.0	475.0/292.74		1200.0/1558.40		45.5/45.0		4.5/1.5		89.92/7.72		0.96/12.48	
554.0	475.0/298.55		1200.0/1533.70		45.7/45.2		4.5/1.5		88.29/10.07		0.84/11.71	
559.0	475.0/299.13		1200.0/1533.13		45.7/45.2		4.5/1.5		88.71/9.52		0.82/11.43	
577.0	475.0/309.71		1200.0/1506.17		45.7/45.2		5.0/1.8		88.97/9.52		0.89/12.43	
583.0	475.0/301.63		1200.0/1512.59		45.7/45.2		5.0/1.8		90.19/8.04		0.93/12.52	
587.0	475.0/299.73		1200.0/1520.99		45.7/45.2		5.0/1.9		90.70/7.50		0.91/12.27	
601.0	475.0/304.32		1200.0/1511.64		45.7/45.2		4.9/1.7		90.44/7.76		0.91/12.27	
607.0	475.0/305.67		1200.0/1504.95		45.7/45.2		5.0/1.8		90.41/7.70		0.93/12.52	
623.0	475.0/299.56		1200.0/1496.57		45.7/45.0		5.0/1.9		88.78/9.24		1.03/13.22	
627.5	475.0/308.18		1200.0/1522.46		45.7/45.2		5.0/1.9		86.85/11.42		0.75/11.06	
633.5	475.0/297.96		1200.0/1548.97		45.7/45.2		5.0/1.9		88.15/9.77		0.82/11.06	
647.5	475.0/293.61		1200.0/1545.68		45.7/45.2		4.7/1.5		90.22/7.78		0.85/11.66	
659.5	475.0/297.64		1200.0/1540.63		45.5/45.0		4.7/1.5		89.76/8.47		0.88/11.75	
671.5	475.0/307.24		1200.0/1527.87		45.5/45.0		4.7/1.5		87.74/11.53		0.80/11.24	
677.5	475.0/299.35		1200.0/1532.22		45.5/45.0		4.7/1.5		89.79/8.86		0.86/11.83	
683.5	475.0/301.48		1200.0/1544.38		45.5/45.0		4.7/1.5		88.81/10.19		0.81/11.46	
696.0	475.0/297.19		1200.0/1532.74		45.0/44.5		4.6/1.5		89.43/9.60		0.84/11.79	
700.0	475.0/297.51		1200.0/1532.89		45.0/44.5		4.6/1.5		89.51/9.37		0.82/11.45	
704.0	475.0/291.67		1200.0/1542.96		45.0/45.0		4.6/1.5		88.48/10.5		0.79/11.26	
708.0	475.0/296.06		1200.0/1538.69		45.0/44.5		4.6/1.5		88.71/9.20		0.82/11.62	
722.0	475.0/300.29		1200.0/1539.37		45.0/44.5		4.6/1.5		88.35/10.41		0.78/11.24	

* Balance Helium; Feed: 41%CO₂-58%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 50 psig; Shell liquid pressurized with helium;
Humidified feed and sweep gas; Average N₂ Recovery: 91%

FIGURE 4-39

CLM STABILITY STUDIES: SWEEP GAS MODE OF OPERATION WITH AQUEOUS 20 WT%
DEA SOLUTION AS A MEMBRANE IN PERMEATORS #11 & #12 IN SERIES

Table 4-64. Here the purified feed gas contained about 24% CO_2 and a N_2 recovery of 99% was obtained. In the second experiment, reported in Table 4-65, a feed gas mixture of 4% CO_2 and 96% N_2 was used at about atmospheric pressure (problem posed by Permapure Products, Inc.). Here the purified gas contained only about 1% CO_2 .

20 wt% DEA Solution as Liquid Membrane and CO_2 - CH_4 Gas Mixture as Feed

Long-term separation studies were carried out over a period of 10 days in Permeator #11 using a gas mixture containing methane and carbon dioxide. The feed gas composition, as determined by GC analysis was 44% CO_2 - 56% CH_4 . Pure N_2 gas was used as a sweep gas.

The feed gas mixture as well as the sweep gas stream were thoroughly humidified as an aqueous solution of 20 wt% DEA was utilized as the liquid membrane. The gas stream humidities, as indicated by the humidity probes, were very close to 100%. Two membrane humidifiers were needed in the sweep line whereas one humidifier in the feed line was sufficient to raise the gas stream humidities to be level of 100%. The bath temperature was kept at 25°C. However, the bath temperature varied considerably during the ten-day run due to the fluctuations in the surrounding temperature. During the evenings and weekends, the air conditioning system was essentially off.

Table 4-66 indicates the flow rates and pressures of various streams. The reaction between CO_2 and DEA is strongly dependent on the temperature. The CO_2 composition in the purified gas stream varied from 12 to 24%. This variation is mostly due to the variation in temperature of the system. The pressure drop in the feed stream was negligible and that of the sweep stream was only about 5 psi for the flow rates used in this study. The average methane recovery was close to 94%. The composition of the feed and sweep outlet streams and the recovery of methane gas for the entire period is shown in Figure 4-40.

The results very strongly support the contention that long-term separation of CO_2 can be carried out efficiently with a high methane recovery in a large-scale hollow-fiber-contained liquid membrane permeator having a 20 wt% DEA in water as a liquid membrane. Higher purification can be achieved with higher

Table 4-64

PURIFICATION RUN WITH MODEL BIOGAS FEED MIXTURE IN SWEEP GAS MODE
AND 20 WT% DEA AS MEMBRANE IN PERMEATORS #11 & #12 IN SERIES

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Composition Percentage	N ₂ /CO ₂ *	Composition Percentage	N ₂ /CO ₂ *
1.5	475.0/375.16		1200.0/1448.93	4.5/1.5		4.5/1.7		4.5/1.7	73.12/24.25		0.21/7.48	
3.5	475.0/377.71		1200.0/1447.78	4.5/1.5		4.5/1.7		4.5/1.7	72.92/24.23		0.25/7.92	
5.5	475.0/377.74		1200.0/1447.94	4.5/1.5		4.5/1.7		4.5/1.7	72.91/24.22		0.25/7.91	
7.5	475.0/377.72		1200.0/1448.17	4.5/1.5		4.5/1.7		4.5/1.7	72.84/24.27		0.22/7.90	
17.5	475.0/379.11		1200.0/1447.53	4.5/1.5		4.5/1.7		4.5/1.7	72.90/24.12		0.22/7.96	
19.5	475.0/378.82		1200.0/1446.53	4.5/1.5		4.5/1.7		4.5/1.7	73.17/24.13		0.22/8.07	
23.5	475.0/375.70		1200.0/1440.29	4.5/1.5		4.5/1.7		4.5/1.7	73.57/23.77		0.22/8.27	
29.5	475.0/377.04		1200.0/1439.76	4.5/1.5		4.5/1.7		4.5/1.7	73.75/23.59		0.24/8.29	
41.5	475.0/376.79		1200.0/1448.97	4.5/1.5		4.5/1.7		4.5/1.7	73.84/23.66		0.22/8.18	
45.5	475.0/376.71		1200.0/1436.37	4.5/1.5		4.5/1.7		4.5/1.7	74.14/23.56		0.22/8.61	
55.5	475.0/375.84		1200.0/1447.05	4.5/1.5		4.5/1.7		4.5/1.7	73.85/24.12		0.21/8.00	

* Balance Helium; Feed: 41%CO₂-58%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 10 psig; Shell liquid pressurized with helium;
Humidified feed and sweep gas; Average N₂ Recovery: 99%

Table 4-65

PURIFICATION RUN WITH MODEL BIOGAS FEED MIXTURE IN SWEEP GAS MODE
AND 20 WT% DEA AS MEMBRANE IN PERMEATORS #11 & #12 IN SERIES

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *	Composition Percentage N ₂ /CO ₂ *
1.5	630.0/570.28	1200.0/1343.77	1200.0/1343.77	5.0/1.0	4.3/1.4	4.3/1.4	4.3/1.4	98.15/0.59	0.42/1.12	0.42/1.12	0.42/1.12	0.42/1.12
3.0	630.0/569.94	1200.0/1347.84	1200.0/1347.84	5.0/1.0	4.3/1.4	4.3/1.4	4.3/1.4	98.44/0.55	0.38/1.14	0.38/1.14	0.38/1.14	0.38/1.14
5.0	630.0/568.94	1200.0/1350.46	1200.0/1350.46	5.0/1.0	4.3/1.4	4.3/1.4	4.3/1.4	98.08/1.03	0.36/1.29	0.36/1.29	0.36/1.29	0.36/1.29
7.0	630.0/570.77	1200.0/1352.95	1200.0/1352.95	5.0/1.0	4.3/1.4	4.3/1.4	4.3/1.4	97.57/1.10	0.40/1.43	0.40/1.43	0.40/1.43	0.40/1.43
9.0	630.0/575.09	1200.0/1348.61	1200.0/1348.61	5.0/1.0	4.3/1.4	4.3/1.4	4.3/1.4	97.78/1.18	0.38/1.45	0.38/1.45	0.38/1.45	0.38/1.45
24.0	630.0/574.09	1200.0/1348.86	1200.0/1348.86	5.0/1.0	4.3/1.4	4.3/1.4	4.3/1.4	98.19/1.27	0.36/1.44	0.36/1.44	0.36/1.44	0.36/1.44

* Balance Helium; Feed: 4%CO₂-96%N₂; Bath Temp.: 25°C; Sweep: Helium;
Shell Press.: 10 psig; Shell liquid pressurized with helium;
Humidified feed and sweep gas; Average N₂ Recovery: 93%

Table 4-66

LONG TERM PURIFICATION RUN WITH MODEL BIOGAS FEED MIXTURE IN SWEEP GAS MODE
AND 20 WT% DEA IN WATER AS A MEMBRANE IN LARGE SCALE PERMEATOR #11

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Sweep Side Flow Rate scc/min		Feed Side Pressure psig		Sweep Side Pressure psig		Feed Outlet Composition Percentage CH ₄ /CO ₂ *		Sweep Outlet Composition Percentage CH ₄ /CO ₂ *	
	Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		CH ₄ /CO ₂ *		CH ₄ /CO ₂ *	
2.0	380.0/193.45		1000.0/1266.14		45.0/45.0		4.90/1.55		83.46/15.12		3.94/10.41	
6.0	380.0/203.46		1000.0/1249.37		45.0/45.0		5.00/1.55		82.81/16.77		3.64/10.47	
9.0	380.0/203.01		1000.0/1251.37		45.0/45.0		5.00/1.55		82.03/17.76		3.49/10.23	
11.5	380.0/201.85		1000.0/1259.55		45.0/45.0		5.00/1.55		82.22/18.19		3.38/ 9.74	
13.5	380.0/201.85		1000.0/1266.03		45.0/45.0		5.00/1.55		82.65/17.80		3.29/10.15	
17.0	380.0/203.16		1000.0/1262.74		45.0/45.0		5.00/1.60		83.41/16.89		3.17/10.15	
21.0	380.0/207.67		1000.0/1256.43		45.0/45.0		5.00/1.60		83.03/16.52		2.98/10.32	
26.0	380.0/215.33		1000.0/1231.45		45.0/45.0		5.00/1.60		86.34/13.48		2.01/11.45	
30.5	380.0/223.52		1000.0/1227.31		45.0/45.0		5.25/1.70		86.29/12.15		1.78/11.37	
34.5	380.0/231.72		1000.0/1218.96		45.0/45.0		5.25/1.70		83.99/16.11		1.16/ 9.58	
38.0	380.0/257.55		1000.0/1202.44		45.0/45.0		5.50/1.75		78.57/21.32		0.90/ 8.74	
42.0	380.0/242.51		1000.0/1219.64		45.0/45.0		5.25/1.75		82.89/16.42		0.99/ 9.45	
46.5	380.0/268.05		1000.0/1191.86		45.0/45.0		5.50/1.75		76.24/23.70		0.82/ 8.66	
50.0	380.0/261.19		1000.0/1195.02		45.0/45.0		5.50/1.80		78.07/21.91		0.90/ 9.25	
54.0	380.0/262.19		1000.0/1195.03		45.0/45.0		5.50/1.75		78.03/21.94		0.91/ 9.28	
58.5	380.0/259.74		1000.0/1203.89		45.0/45.0		5.50/1.70		77.46/22.33		0.85/ 8.68	
62.0	380.0/263.92		1000.0/1200.74		45.0/45.0		5.10/1.75		77.30/22.40		0.83/ 8.48	
66.0	380.0/255.00		1000.0/1215.65		45.0/45.0		5.20/1.50		78.20/21.15		0.92/ 9.14	
70.5	380.0/260.96		1000.0/1198.60		45.0/45.0		5.50/1.50		77.84/21.86		0.89/ 9.11	
72.5	380.0/264.62		1000.0/1192.22		45.0/45.0		5.50/1.50		77.34/22.45		0.88/ 9.03	
76.5	380.0/266.70		1000.0/1189.80		45.0/45.0		5.25/1.70		76.63/23.10		0.86/ 8.94	
79.5	380.0/259.10		1000.0/1199.48		45.0/45.0		5.25/1.60		78.40/21.27		0.96/ 9.50	
83.5	380.0/255.10		1000.0/1204.21		45.0/45.0		5.25/1.60		78.40/21.27		0.99/ 9.78	
87.5	380.0/263.81		1000.0/1213.01		45.0/45.0		5.25/1.60		78.51/20.17		0.86/ 9.00	
91.5	380.0/263.71		1000.0/1230.22		45.0/45.0		5.25/1.60		77.98/21.79		0.92/ 9.38	

Table 4-66 (cont.)

Elapsed Time hrs.	Feed Side Flow Rate scc/min		Sweep Side Flow Rate scc/min		Feed Side Pressure psig		Sweep Side Pressure psig		Feed Outlet Composition Percentage CH ₄ /CO ₂ *		Sweep Outlet Composition Percentage CH ₄ /CO ₂ *	
	Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		Inlet/Outlet		CH ₄ /CO ₂ *		CH ₄ /CO ₂ *	
95.0	380.0/257.88		1000.0/1238.49		45.0/45.0		5.00/1.60		79.31/20.47		0.96/ 9.56	
98.0	380.0/259.93		1000.0/1239.58		45.0/45.0		5.25/1.60		79.78/19.99		0.96/ 9.50	
102.0	380.0/265.58		1000.0/1237.46		45.0/45.0		5.20/1.60		77.78/22.03		0.86/ 8.94	
105.0	380.0/267.26		1000.0/1234.96		45.0/45.0		5.20/1.60		77.06/22.83		0.84/ 8.80	
109.5	380.0/263.16		1000.0/1243.55		45.0/45.0		5.20/1.60		76.29/23.30		0.79/ 8.37	
112.0	380.0/263.78		1000.0/1243.64		45.0/45.0		5.25/1.60		76.04/23.31		0.80/ 8.42	
114.5	380.0/266.20		1000.0/1248.46		45.0/45.0		5.20/1.60		76.24/22.95		0.83/ 8.86	
117.0	380.0/263.83		1000.0/1226.92		45.0/45.0		5.20/1.60		77.97/21.40		0.91/ 9.59	
120.5	380.0/266.96		1000.0/1190.76		45.3/45.3		5.20/1.60		79.25/20.11		0.86/ 9.08	
125.0	380.0/257.01		1000.0/1205.64		45.2/45.2		5.20/1.60		78.27/21.07		0.97/ 9.80	
128.0	380.0/265.68		1000.0/1189.69		45.2/45.2		5.20/1.60		77.73/21.70		0.84/ 9.00	
132.0	380.0/268.22		1000.0/1199.76		45.0/45.0		5.25/1.60		75.93/23.61		0.77/ 8.52	
135.5	380.0/269.27		1000.0/1206.38		45.0/45.0		5.25/1.68		75.38/23.77		0.77/ 8.55	
137.5	380.0/263.70		1000.0/1214.53		45.0/45.0		5.30/1.65		76.39/22.65		0.82/ 8.86	
140.0	380.0/265.67		1000.0/1205.56		45.0/45.0		5.00/1.60		77.24/21.83		0.84/ 9.11	
143.0	380.0/271.10		1000.0/1198.17		45.0/45.0		5.20/1.60		77.58/21.69		0.81/ 8.81	
146.5	380.0/269.15		1000.0/1210.02		45.2/45.2		5.20/1.60		76.51/22.71		0.83/ 9.08	
149.5	380.0/266.58		1000.0/1224.31		45.3/45.3		5.20/1.60		77.49/21.60		0.86/ 9.25	
152.0	380.0/264.64		1000.0/1197.65		45.2/45.2		5.25/1.65		78.11/20.99		0.90/ 9.57	
155.0	380.0/263.04		1000.0/1204.10		45.2/45.2		5.25/1.65		78.18/21.16		0.79/ 8.74	
158.0	380.0/267.81		1000.0/1203.63		45.2/45.2		5.20/1.60		75.48/23.85		0.78/ 8.84	
160.0	380.0/262.58		1000.0/1207.20		45.2/45.2		5.20/1.63		76.85/22.25		0.81/ 9.08	
162.5	380.0/268.63		1000.0/1201.10		45.2/45.2		5.20/1.60		76.25/22.80		0.75/ 8.61	
164.5	380.0/268.12		1000.0/1207.70		45.0/45.0		5.00/1.60		75.74/23.12		0.78/ 8.90	
167.0	380.0/263.89		1000.0/1208.12		45.0/45.0		5.00/1.60		77.19/21.79		0.88/ 9.72	
170.0	380.0/250.45		1000.0/1212.20		45.0/45.0		5.00/1.60		81.42/17.50		1.02/10.47	
173.0	380.0/271.28		1000.0/1187.81		45.3/45.3		5.10/1.60		77.55/21.66		0.74/ 8.73	

Table 4-66 (cont.)

Elapsed Time hrs.	Feed Side		Sweep Side		Feed Side		Sweep Side		Feed Outlet		Sweep Outlet	
	Flow Rate scc/min	Inlet/Outlet	Flow Rate scc/min	Inlet/Outlet	Pressure psig	Inlet/Outlet	Pressure psig	Inlet/Outlet	Composition Percentage CH ₄ /CO ₂ *	Composition Percentage CH ₄ /CO ₂ *	Composition Percentage CH ₄ /CO ₂ *	Composition Percentage CH ₄ /CO ₂ *
176.0	380.0/275.77		1000.0/1190.45		45.3/45.3		5.10/1.50		75.59/23.71		0.77/ 8.98	
178.0	380.0/265.25		1000.0/1203.52		45.5/45.5		5.00/1.45		76.52/22.68		0.79/ 9.14	
180.5	380.0/262.81		1000.0/1206.10		45.5/45.5		5.00/1.35		77.10/21.94		0.77/ 8.85	
182.0	380.0/262.82		1000.0/1202.82		45.5/45.5		5.00/1.35		76.87/22.17		0.76/ 8.71	
185.0	380.0/266.90		1000.0/1211.38		45.5/45.5		5.00/1.40		76.19/22.79		0.71/ 8.46	
186.5	380.0/268.06		1000.0/1212.86		45.0/45.0		5.00/1.60		75.86/23.06		0.69/ 8.33	
189.5	380.0/267.25		1000.0/1212.05		45.0/45.0		5.00/1.60		76.17/22.68		0.76/ 9.04	
192.5	380.0/239.10		1000.0/1237.33		45.2/45.2		5.00/1.40		84.28/14.48		0.99/10.65	
193.5	380.0/239.16		1000.0/1227.48		45.3/45.3		5.00/1.35		85.80/13.01		1.02/10.70	
196.0	380.0/249.33		1000.0/1216.41		45.5/45.5		5.00/1.35		83.09/15.97		0.93/10.25	
200.0	380.0/257.19		1000.0/1206.49		45.5/45.5		5.00/1.60		80.64/18.77		0.84/ 9.82	
203.0	380.0/239.48		1000.0/1224.19		45.5/45.5		5.20/1.60		82.71/16.70		0.97/10.64	
205.5	380.0/241.55		1000.0/1228.29		45.5/45.5		5.20/1.60		82.31/17.06		0.93/10.26	
208.0	380.0/237.77		1000.0/1238.43		45.5/45.5		5.20/1.60		83.82/15.12		0.95/10.31	
211.0	380.0/243.39		1000.0/1219.59		45.5/45.5		5.20/1.60		79.89/19.52		0.90/ 9.88	
216.0	380.0/262.53		1000.0/1203.41		45.5/45.5		5.30/1.60		76.02/23.82		0.79/ 9.74	
218.0	380.0/243.82		1000.0/1220.10		45.5/45.5		5.30/1.60		81.30/18.31		0.95/10.46	
221.0	380.0/268.71		1000.0/1195.86		45.5/45.5		5.40/1.70		78.11/21.72		0.66/ 8.57	
224.0	380.0/241.93		1000.0/1226.10		45.5/45.5		5.40/1.70		82.53/17.07		0.85/10.10	
226.0	380.0/258.11		1000.0/1205.31		45.5/45.5		5.20/1.60		81.12/18.71		0.74/ 9.32	
230.0	380.0/262.59		1000.0/1208.11		45.5/45.5		5.20/1.60		75.85/23.98		0.61/ 8.24	
232.0	380.0/250.53		1000.0/1222.84		45.5/45.5		5.20/1.50		80.98/18.33		0.81/ 9.76	
235.0	380.0/248.03		1000.0/1219.57		45.5/45.5		5.20/1.40		82.01/17.16		0.77/ 9.38	
237.0	380.0/270.63		1000.0/1201.65		45.5/45.5		5.20/1.40		77.56/21.91		0.63/ 8.62	
239.0	380.0/260.76		1000.0/1197.42		45.5/45.5		5.20/1.40		79.48/20.03		0.74/ 9.35	

* Balance Nitrogen; Feed: 44%CO₂-56%CH₄; Bath Temp.: 25°C; Sweep: Nitrogen;
 Shell Press.: 50 psig; Shell liquid pressurized with helium;
 Humidified feed and sweep gas; Average CH₄ Recovery: ~94%

FIGURE 4-40

CLM STABILITY STUDIES: SWEEP GAS MODE OF OPERATION

WITH AQUEOUS 20 WT% DEA SOLUTION AS A MEMBRANE IN PERMEATOR #11

membrane area and a better membrane permeator with a lower thickness of membrane.

BEST PERFORMANCES UNDER DIFFERENT MODES OF OPERATION

It has been shown that the operational flexibility of a permeator increases substantially with the new HFCLM technology. In the small-scale operation, the new technique was applied to separate a model biogas feed mixture under a variety of operating modes; these include sweep gas, sweep liquid, vacuum and conventional permeation. We have demonstrated that the HFCLM system can be applied successfully under all modes of operation. The best separation performances observed under different operating modes in small-scale operation are summarized in Table 4-67. The operating conditions, purified gas compositions and the recovery in a given operating mode are shown in the table.

Table 4-67

BEST PERFORMANCES IN DIFFERENT OPERATING MODES

Mode Parameter	20% DEA SOLUTION		PURE WATER		MEMBRANE LIQUID	
	Sweep Gas	Sweep Water	Sweep Gas	Conven- tional	Vacuum	Sweep Water
Permeator No.	8	8	6 & 7	3	3	6
Length inches	17	17	48	62	62	24
Feed Gas Composition	40% CO ₂ - 60% CH ₄	40% CO ₂ - 60% N ₂	40% CO ₂ - 60% CH ₄	40% CO ₂ - 60% N ₂	40% CO ₂ - 60% N ₂	40% CO ₂ - 60% N ₂
Sweep Fluid	N ₂	Water	N ₂	None	None	Water
Feed Gas Flow Rate, sccm	50	40	50	50	100	50
Sweep/Permeate Inlet Flow Rate	200 sccm	30 cc/m	350 sccm	-	-	116 cc/m
Feed Inlet Pressure	45 psig	45 psig	45 psig	45 psig	30 psig	45 psig
Sweep/Permeate Inlet Pressure	6.2 psig	49 psig	6.5 psig	6.7 psig	17.0 in Hg	20 psig
Sweep/Permeate Outlet Pressure	2 psig	0 psig	2 psig	2 psig	0.7 in Hg	0 psig
Feed Outlet Composition % CO ₂ /N ₂ or CH ₄	7.0/92.0	9.5/90.5	5.5/92.0	5.0/95.0	4.0/96.0	9.5/90.5
CH ₄ or N ₂ Recovery ² (%)	93	98	87	72	83	97

Section 5

PRELIMINARY ECONOMIC ANALYSIS

A comparative economic analysis of different modes of HFCLM operation for biogas purification has been carried out here. The purpose of this exercise is to guide our selection of the optimum mode of operation rather than determine the actual cost of purification by such a process. The following five modes have been considered for preliminary calculations:

- Mode 1 : Sweep mode of operation with air as sweep gas and 20% DEA solution as membrane liquid
- Mode 2 : Sweep mode of operation with air as sweep gas and water as membrane liquid
- Mode 3 : Conventional mode of operation with pure water as membrane
- Mode 4 : Vacuum mode of operation with pure water liquid membrane
- Mode 5 : Sweep water mode of operation with pure water membrane

Modes 2, 3, 4 and 5 allow a direct comparison of the different modes for pure permeation through a given liquid. For all modes, it was considered that 1 million std cft/day (MSCFD) of biogas (composition: 40% CO₂ - 60% CH₄) had to be upgraded to pipeline quality. The operating parameters, utilized for preliminary analysis, are summarized in Table 5-1. These projections were based on our experimental observations.

The estimated production cost under various modes (i. e., 1, 2, 3, 4 and 5) are shown in Tables 5-2, 5-3, 5-4, 5-5 and 5-6, respectively. All discussions pertain to a product gas purity of 95% methane. For simplicity, raw feed gas was assumed to be available at no cost. The estimated cost of membrane area, utility etc. are shown at the bottom of the Table 5-2. The same values were used for production cost calculation of other modes. The sizes and costs of compressor, blower, pump and vacuum pump were determined from Peters and Timmerhaus (1980), Evans (1979) and Matley (1984, 1977).

It is obvious that the cost of purification is the lowest for 20% aqueous DEA solution. It is also obvious that the capital as well as operating cost of

TABLE 5-1

SUMMARY OF PARAMETERS FOR A COMPARATIVE ECONOMIC ANALYSIS OF
DIFFERENT OPERATING MODES

Mode Parameter	Sweep Air with 20% DEA Sol.	PURE Sweep Air	WATER Conven- tional	MEMBRANE Vacuum	LIQUID Sweep Water
Feed Gas Processing Capacity (MSCFD) ¹	1	1	1	1	1
Sweep Fluid	Air	Air	None	None	Water
Feed Inlet Pressure (Atm)	4	4	4	4	4
Sweep/Permeate Outlet Pressure (Atm)	1	1	1	0.07	1
Sweep/Permeate Inlet Pressure (Atm)	1.5	3	2	0.5	3
Sweep/Permeate Inlet Flow Rate	4 MSCFD	3 MSCFD	-	-	1700 CFM ²
Maximum Impurity in Product (%)	5	5	5	5	5
Methane Recovery (%)	95	80	70	85	95

1. MSCFD = million standard cubic feet per day

2. CFM = cubic feet per minute

TABLE 5-2

ECONOMIC CHARACTERISTICS OF SWEEP GAS MODE OF OPERATION WITH
20% DEA SOLUTION AS MEMBRANE

Item	Size	Number	Cost (\$1,000)
1. Fixed Capital Cost			
1.1 Process Equipment			
- Membrane Module ^a	1 $\frac{1}{2}$ ' (L) X 16" (D)	100	550
- Single Stage Gas Compressor with Gas Fired Engine	100 hp	1	70
- Centrifugal Blower	100 hp	1	21
- Subtotal of 1.1			<u>641</u>
1.2 Piping, Instrumentation and Installation ^b			430
1.3 Total of 1.1 and 1.2			<u>1,071</u>
2. Manufacturing Cost per Year			
2.1 Utility ^c			115
2.2 Labor ^d			210
2.3 Total of 2.1 and 2.2			<u>325</u>
3. Total Product Price ^e per Year			<u>1,420</u>

a \$1.00 per ft² of membrane area

b estimated by multiplying the item of 1.1 by 2/3

c \$0.088 per Kw-Hr

d \$12.00 per Man-Hour, 2 persons

e \$0.65 per 100 ft³ of 95% CH₄ natural gas

TABLE 5-3
ECONOMIC CHARACTERISTICS OF SWEEP GAS MODE OF OPERATION

Item	Size	Number	Cost (\$1,000)
1. Fixed Capital Cost			
1.1 Process Equipment			
- Membrane Module	5' (L) X 16" (D)	48	900
- Single Stage Gas Compressor with Gas Fired Engine	100 hp	1	70
- Centrifugal Blower	300 hp	1	25
- Subtotal of 1.1			<u>995</u>
1.2 Piping, Instrumentation and Installation			<u>663</u>
1.3 Total of 1.1 and 1.2			<u>1,658</u>
2. Manufacturing Cost per Year			
2.1 Utility			<u>230</u>
2.2 Labor			<u>210</u>
2.3 Total of 2.1 and 2.2			<u>440</u>
3. Total Product Price per Year			<u>1,200</u>

TABLE 5-4

ECONOMIC CHARACTERISTICS OF CONVENTIONAL MODE OF OPERATION

Item	Size	Number	Cost (\$1,000)
1. Fixed Capital Cost			
1.1 Process Equipment			
- Membrane Module	5'(L) X 16"(D)	96	1,800
- Single Stage Gas Compressor with Gas Fired Engine	100 hp	1	70
- Subtotal of 1.1			<u>1,870</u>
1.2 Piping, Instrumentation and Installation			<u>1,247</u>
1.3 Total of 1.1 and 1.2			<u>3,117</u>
2. Manufacturing Cost per Year			
2.1 Utility			<u>58.4</u>
2.2 Labor			<u>210.0</u>
2.3 Total of 2.1 and 2.2			<u>268.4</u>
3. Total Product Price per Year			<u>1,050</u>

TABLE 5-5
ECONOMIC CHARACTERISTICS OF VACUUM MODE OF OPERATION

Item	Size	Number	Cost (\$1,000)
1. Fixed Capital Cost			
1.1 Process Equipment			
- Membrane Module	5' (L) X 16" (D)	48	900
- Single Stage Gas Compressor with Gas Fired Engine	100 hp	1	70
- Reciprocating Mechanical Vacuum Pump with Explosion Proof Motor	250 hp	1	48
- Subtotal of 1.1			<u>1,018</u>
1.2 Piping, Instrumentation and Installation			<u>679</u>
1.3 Total of 1.1 and 1.2			<u>1,697</u>
2. Manufacturing Cost per Year			
2.1 Utility			<u>201</u>
2.2 Labor			<u>210</u>
2.3 Total of 2.1 and 2.2			<u>411</u>
3. Total Product Price per Year			<u>1,270</u>

TABLE 5-6

ECONOMIC CHARACTERISTICS OF SWEEP WATER MODE OF OPERATION

Item	Size	Number	Cost (\$1,000)
1. Fixed Capital Cost			
1.1 Process Equipment			
- Membrane Module	2'(L) X 16"(D)	125	900
- Single Stage Gas Compressor with Gas Fired Engine	100 hp	1	70
- Cast Steel Casing Inline Horizontal Motor and Centrifugal pump	200 hp	2	30
- Subtotal of 1.1			<u>1,000</u>
1.2 Piping, Instrumentation and Installation			<u>667</u>
1.3 Total of 1.1 and 1.2			<u>1,667</u>
2. Manufacturing Cost per Year			
2.1 Utility			<u>288</u>
2.2 Labor			<u>210</u>
2.3 Total of 2.1 and 2.2			<u>498</u>
3. Total Product Price per Year			<u>1,420</u>

purification for sweep air (Table 5-3), vacuum mode (Table 5-5) are quite close. However, the sweep water mode yields higher product price because of higher methane recovery.

Section 6

INTERACTIONS WITH CORPORATIONS REGARDING HFCLM TECHNOLOGY

As part of project task H requiring the contractor to acquaint corporations about the value and possible usefulness of this technology, a number of corporations have been contacted during 1988-1989. The objectives included possible commercialization of the hollow-fiber-contained liquid membrane technique for separation of gas mixtures in general as well as application of this technology for biogas separation/ CO_2 elimination in particular. Many corporations were sent a copy of our first paper (AIChE J., 34(7), 1135-1148, 1988) along with the information that a U.S. patent has been issued to us for both process concepts and apparatus (US Patent NO. 4,750,918, dated June 14, 1988).

The following corporations have expressed an interest/or continuing discussions with us/or visited our laboratories for licensing purposes or collaborative activities leading to licensing.

COMMENTS

1. Permapure Products, Inc.
8 Executive Dr.
Toms River, NJ 08754
Contact: Mr. Jack Kertzman
Tel.No.: 201-244-0010

They have reviewed
our patent and papers.
Visited Stevens on
August 17, 1989.

Discussions continuing for possible medical application of the technique for removing CO_2 . An experiment has been carried out to simulate the exact conditions of application.

2. Air Products and Chemicals, Inc.
Allentown, PA, 18195
Contact: Dr. Daniel V. Laciak
Dr. V. Raman
Tel.No.: (215)481-7889
(215)481-8336

Visited Stevens on
August 8, 1989.
Further visits
planned.

They are thoroughly familiar with our patents and published papers. They are

experimenting with HFCLM modules in their laboratory. These modules were purchased from Hoechst Celanese Corporation, Charlotte, N.C., 28224. They have approached us for making larger scale modules (not available from Hoechst Celanese at this time). If their evaluation is successful, chances for licensing technology to them is very high. It has been directly stated to us by Dr. Laciak.

3. Hoechst Celanese Corporation	They are quite familiar
Separations Products Division	with our work at the
13800 S. Lakes Dr.	published level.
Charlotte, NC, 28224	
Contact: Dr. Robert W. Callahan	
Tel.No.: (704)588-5310	

Hoechst Celanese has started marketing since late 1988 HFCLM modules of small sizes. They have encountered very good response from the market. They have acquired rights from Stevens to use these modules for liquid separations in the middle of 1985. However, recently, they have sold a number of these modules also for gas separation (e.g. to Air Products and Chemicals, Inc.). After recent telephone conversations, Hoechst Celanese has indicated that they are going to open conversations with Stevens (Dr. Stella Manne of Stevens Research Office) regarding licensing. Two items are of interest in this licensing discussion: (1) Large scale HFCLM permeator fabrication techniques developed under NYSERDA-NYGAS-GRI contract: These techniques are useful for both gas and liquid separations; (2) Licensing of HFCLM technique (process and/or apparatus) patent to Hoechst Celanese for gas separation.

4. Ecolotrol	They have reviewed
1300 Shames Drive,	our patent and
Westbury, NY 11590	AICHe J. papers.
Contact: Roger Owens	
Tel.No.: 516-997-2211	

We have had several contacts with Ecolotrol. Roger Owens has suggested the problem of removing CO_2 from an essentially 40% CO_2 -60% N_2 stream coming out at 4-6 inches of water gauge from a denitrification bioreactor. The flow rate is about 35 ft^3/min . He would like to know an estimate of cost of removing CO_2 and recirculating the N_2 back into the bioreactor. One could use air as a

sweep gas or use a vacuum or use water as a sweep liquid. Experiments have been done recently with helium as a sweep gas and N_2 - CO_2 (60-40) feed gas in our large scale setup with 20% aqueous DEA solution as the liquid membrane. The results are excellent. Helium was present only to the extent of 2% in the purified N_2 . This indicates that the amount of O_2 in purified N_2 will be less than 0.3% if air is used as a sweep gas (required for denitrification). Some calculations will be done and communicated to them. If found reasonable, this may be the basis for onsite studies with a slip stream after their denitrification reactor is ready.

5. Biothane
2500 Broadway,
Camden, NJ 08104
Contact: Dr. Robert Sax
Tel.No.: (609)541-3500

Paper (AIChE J.) sent.
They are supposed to be
evaluating the process
and will get back to us
when ready.

6. Purac Engineering
100 Crossways Park West
Woodbury, LI 11797
Contact: William Borkoski
Tel.No.: (302)239-9431

Paper (AIChE J.)
sent. They are
evaluating the process.

Efforts to get this technology licensed out will continue after the completion of the current project. It appears though that a critical stage has been reached. The opening up of licensing discussions with Hoechst Celanese with Air Products and Chemicals Inc. in the backdrop is most promising. Dr. Callahan of Hoechst Celanese indicated that they ought to be satisfying the needs of Air Products and Chemicals and other corporations rather than Stevens building modules for Air Products and Chemicals. In this sense, HFCLM technique is the most desired item in their mind rather than a specific application. A most recent presentation of ours on the long term stability of larger HFCLM permeators apparently has clinched the remaining issues about this technique.

Section 7

NOMENCLATURE

Sometimes more common units are used for clarity. The actual units used on any occasion are stated in the text.

A_f	: total feed side permeation area in HFCLM permeator, m^2
A_m	: flat membrane area, m^2
B_j	: dimensionless quantity defined by Eq. (2-57)
C_3, C_4	: dimensionless concentrations, defined by Eq. (2-113)
C_a, C_b	: local bulk concentration of CO_2 and N_2 (or CH_4), respectively, in sweep water, mole/ m^3
C_i^s	: local bulk concentration of gas species i in sweep water, mole/ m^3
C_a^*, C_b^*	: dimensionless concentrations, defined by Eq. (2-67)
C_T	: initial concentration of DEA, mole/ m^3
d	: liquid membrane thickness, m
D_{FI}, D_{FO}	: inside and outside diameters of microporous hollow feed fibers, m
D_{R_2NH}	: diffusion coefficient of DEA, m^2/sec
D_{SI}, D_{SO}	: inside and outside diameters of microporous hollow sweep (or permeate) fibers, m
D_{iAm}	: diffusion coefficient of gas species i in aqueous DEA solution, m^2/sec
D_{iw}	: diffusion coefficient of gas species i in pure water, m^2/sec
f_{1i}	: dimensionless quantity defined by Eq. (2-53)
f_{2i}	: dimensionless quantity defined by Eq. (2-55)
F_{Am}	: facilitation factor defined by Eq. (2-121)
H_{iAm}	: solubility of gas species i in aqueous DEA solution, mole/ m^3 -Pa
H_{iw}	: solubility of gas species i in pure water, mole/ m^3 -Pa
k_{Am}	: forward reaction rate constant of Eq. (2-97), $m^3/kmole/sec$
$(k_m)_a, (k_m)_b$	: mass transfer coefficient for CO_2 and N_2 (or CH_4) absorption in sweep water, respectively, m/sec
$(k_m)_i _1$	: local mass transfer coefficient of gas species i for absorption in sweep water, m/sec
$(k_m)_i _{avg}$	: average mass transfer coefficient of gas species i for absorption in sweep water, m/sec

K_{Am}	: equilibrium constant of Eq. (2-97)
$(K_{OL})_i$	: overall mass transfer coefficient of gas species i defined by Eq. (4-7), m/sec
K_p	: equilibrium constant of Eq. (2-98), $m^3/kmole$
l	: distance of any permeator location, starting from the feed outlet end, m
l_t	: total length of permeation in a permeator, m
L, L_f, L_w	: feed side gas flow rate per fiber at any location, at the feed inlet end, and at the feed outlet end of the permeator, respectively, mole/sec
L_{ref}	: reference flow rate per fiber, mole/sec
L^*, L_f^*, L_w^*	: dimensionless feed side gas flow rate per fiber at any location, at the feed inlet end, and at the feed outlet end of the permeator, respectively
M_{wi}	: molecular weight of gas species i , kg/mol
N_{CO_2}	: flux of CO_2 , mole/ m^2 -sec
N_F, N_S	: total number feed fibers and sweep fibers, respectively, in a bundle
N_{Gz}	: Graetz number
N_{R_2NH}	: flux of DEA, mole/ m^2 -sec
N_{Re}	: Reynolds number
N_{Sc_i}	: Schmidt number for i -th species
$(N_{Sh_i})_l$	: local Sherwood number
$(N_{Sh_i})_{avg}$	: average Sherwood number
p, p_f, p_w	: sweep (or permeate) side pressure at any location, at the sweep (or permeate) outlet end, and at the sweep inlet (or closed) end of the permeator, respectively, Pa
p_i	: local pressure of the permeate gas inside the pore of a sweep fiber for sweep water mode of operation, Pa
p_w, p_{wf}, p_{ww}	: sweep water pressure at any location, at the sweep outlet end, and at the sweep inlet end of the permeator, respectively, Pa
P, P_f, P_w	: feed side gas pressure at any location, at the feed inlet end, and at the feed outlet end of the permeator, respectively, Pa
P_d, P_u	: downstream and upstream partial pressures of CO_2 across the liquid membrane, respectively, Pa
P_{ref}	: reference pressure, Pa

- q : sweep water flow rate per fiber, m^3/sec
 q_1, q_2, q_3, q_4 : dimensionless parameters defined by Eqs. (2-114), (2-115), (2-116) and (2-117), respectively
 Q_a, Q_b, Q_c : permeability of CO_2 , N_2 (or CH_4) and He (or N_2), respectively, $\text{mole-m/m}^2\text{-sec-Pa}$
 Q_i : permeability of species i , $\text{mole-m/m}^2\text{-sec-Pa}$
 Q_{1Am} : permeability of CO_2 in aqueous solution of DEA, $\text{mole-m/m}^2\text{-sec-Pa}$
 Q_{iAm} : permeability of species i in aqueous solution of DEA, $\text{mole-m/m}^2\text{-sec-Pa}$
 Q_{ref} : reference permeability, $\text{mole-m/m}^2\text{-sec-Pa}$
 r_i : rate of reaction of species i
 r_+ : dimensionless radius used in Eq. (2-53)
 R : universal gas constant, $\text{m}^3\text{-Pa/mole-}^\circ\text{K}$
 R_a, R_b : dimensionless parameters, defined in Eqs. (2-71) and (2-72), respectively
 R_i : permeation rate of gas species i , mole/sec
 R_{Ti} : total permeation rate of gas species i , mole/sec
 s : dimensionless quantity, defined in Eq. (2-68)
 S : dimensionless area, defined by Eq. (2-17)
 S_a, S_b : solubility of CO_2 and N_2 (or CH_4) in sweep water, respectively, $\text{mole/m}^3\text{-Pa}$
 S_t : total dimensionless area
 t_m : thickness of flat membrane, m
 T : absolute temperature, $^\circ\text{K}$
 u, u_f, u_w : mole fraction of He (or N_2) in the feed side gas mixture at any location, at the feed inlet end, and at the feed outlet end of the permeator, respectively
 v, v_f, v_w : mole fraction of He (or N_2) in the sweep side gas mixture at any location, at the sweep outlet end, and at the sweep inlet end of the permeator, respectively
 V, V_f, V_w : sweep (or permeate) side gas flow rate per fiber at any location, at the sweep (or permeate) outlet end, and at the sweep inlet (or closed) end of the permeator, respectively, mole/s
 V^*, V_f^*, V_w^* : dimensionless sweep (or permeate) side gas flow rate per fiber at any location, at the sweep (or permeate) outlet end, and at the sweep inlet (or closed) end of the permeator, respectively

- x, x_f, x_w : mole fraction of CO_2 in the feed side gas mixture at any location, at the feed inlet end, and at the feed outlet end of the permeator, respectively
 y, y_f, y_w : mole fraction of CO_2 in the sweep (or permeate) side gas mixture at any location, at the sweep outlet (or permeate) end, and at the sweep inlet (or closed) end of the permeator, respectively
 y_i : local mole fraction of CO_2 inside the pore of a sweep fiber for sweep water mode of operation, Pa
 z_i : local mole fraction of i -th component in a mixture

Greek Symbols

- ψ_1, ψ_2 : dimensionless parameters, defined in Eqs. (2-79) and (2-80), respectively
 α : dimensionless quantity, defined in Eq. (2-68)
 $\alpha_a, \alpha_b, \alpha_c$: dimensionless permeabilities of CO_2 , N_2 (or CH_4), and He (or N_2), respectively, defined by Eq. (2-21)
 α_{ij} : selectivity between species i and j , defined by Eq. (4-8)
 β : dimensionless parameter, defined in Eq. (2-22)
 β_F, β_S : dimensionless parameters, defined in Eqs. (2-69) and (2-70), respectively
 β_j : dimensionless parameter, defined in Eq. (2-56)
 ξ : dimensionless membrane thickness, defined in Eq. (2-113)
 γ_1, γ_2 : dimensionless feed gas pressure and sweep gas (or permeate) pressure, respectively, defined by Eq. (2-18)
 γ_w, γ_i : dimensionless pressures, defined by Eq. (2-66)
 γ_{1f}, γ_{1w} : dimensionless pressures at feed gas inlet end and feed gas outlet end, respectively
 γ_{2f}, γ_{2w} : dimensionless pressures at sweep gas (or permeate) outlet end and sweep gas inlet (or closed) end, respectively
 γ_{wf}, γ_{ww} : dimensionless pressures at sweep water outlet end and sweep water inlet end, respectively
 $(\Delta C_{\text{avg}})_i$: area averaged concentration difference of i -th species, mole/m^3 defined by Eq. (4-7)
 ΔP_i : partial pressure difference of i -th species, Pa
 $\varepsilon, \varepsilon_m$: hollow fiber and flat film porosities

ϕ_j : defined in Eq. (2-57)
 θ : dimensionless parameter, defined in Eq. (2-6)
 μ_{Am} : viscosity of aqueous DEA solution, Pa-sec
 μ_i : viscosity of gas species i, Pa-sec
 μ_F, μ_S, μ_P : viscosity of feed, sweep and permeate gas mixture, respectively,
at any location of the permeator, Pa-sec
 μ_{ref} : reference viscosity, Pa-sec
 μ_w : viscosity of water, Pa-sec
 $\mu_F^*, \mu_S^*, \mu_P^*$: dimensionless viscosity of feed, sweep and permeate gas mixture,
respectively, at any location of the permeator, defined in Eq.
(2-20)
 $\bar{\mu}$: viscosity of gas mixture, defined by Eq. (2-31), Pa-sec
 π : 3.14159...
 τ_m : tortuosity of flat membrane
 ϕ_{ij} : constants arising in gas mixture viscosity estimation, defined in
Eq. (2-32)

Section 8

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