

2. History of Membrane Development and Mass Transfer Modelling

(Takeshi Matsuura, Prof. Matsuura, IMRI,
Univ. of Ottawa)

HISTORY OF MEMBRANE DEVELOPMENT

Presented at

The Fourth Membrane Society of Korea Workshop

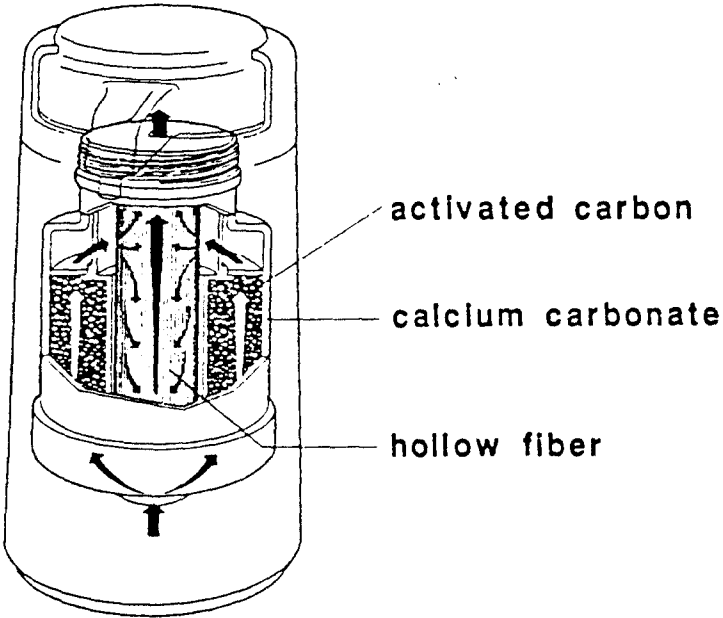
By

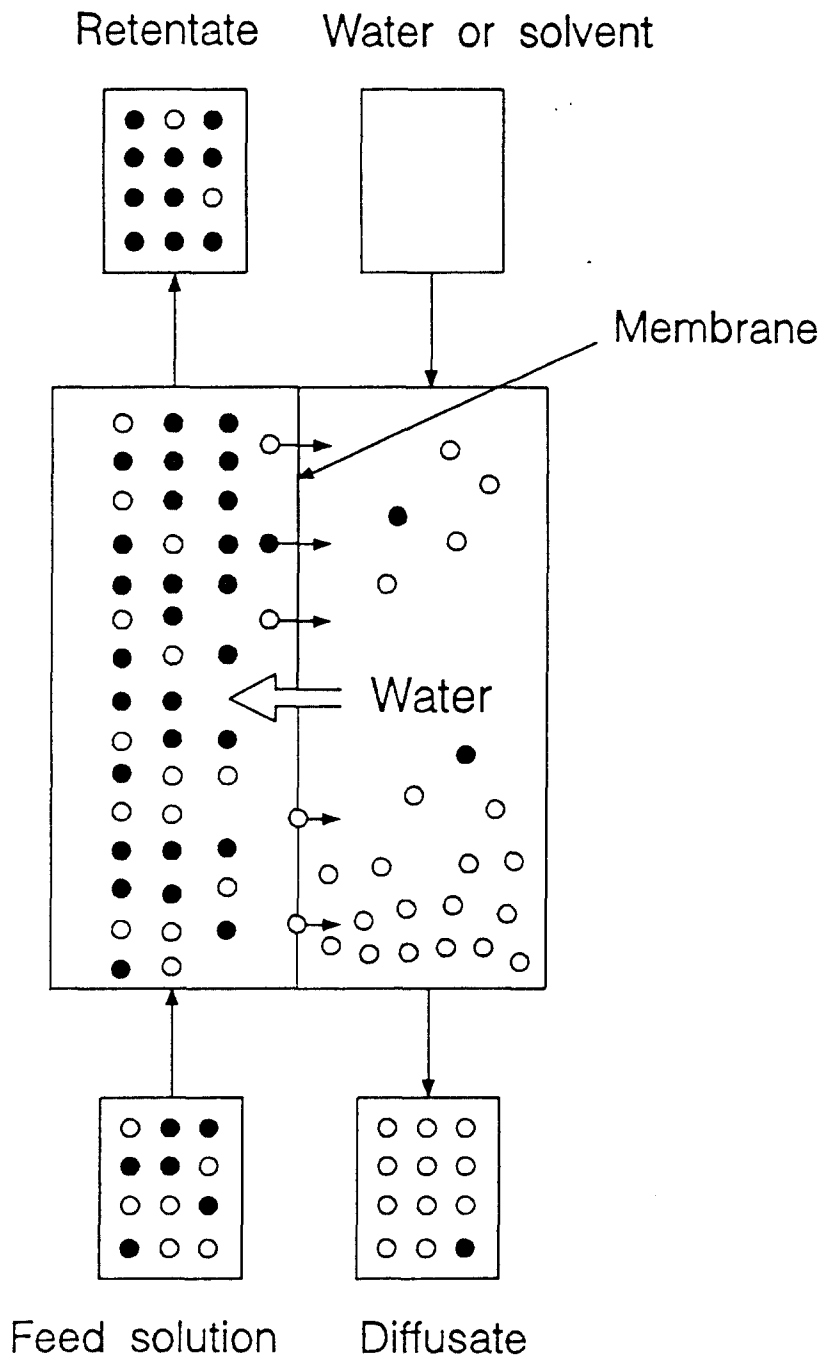
Takeshi Matsuura

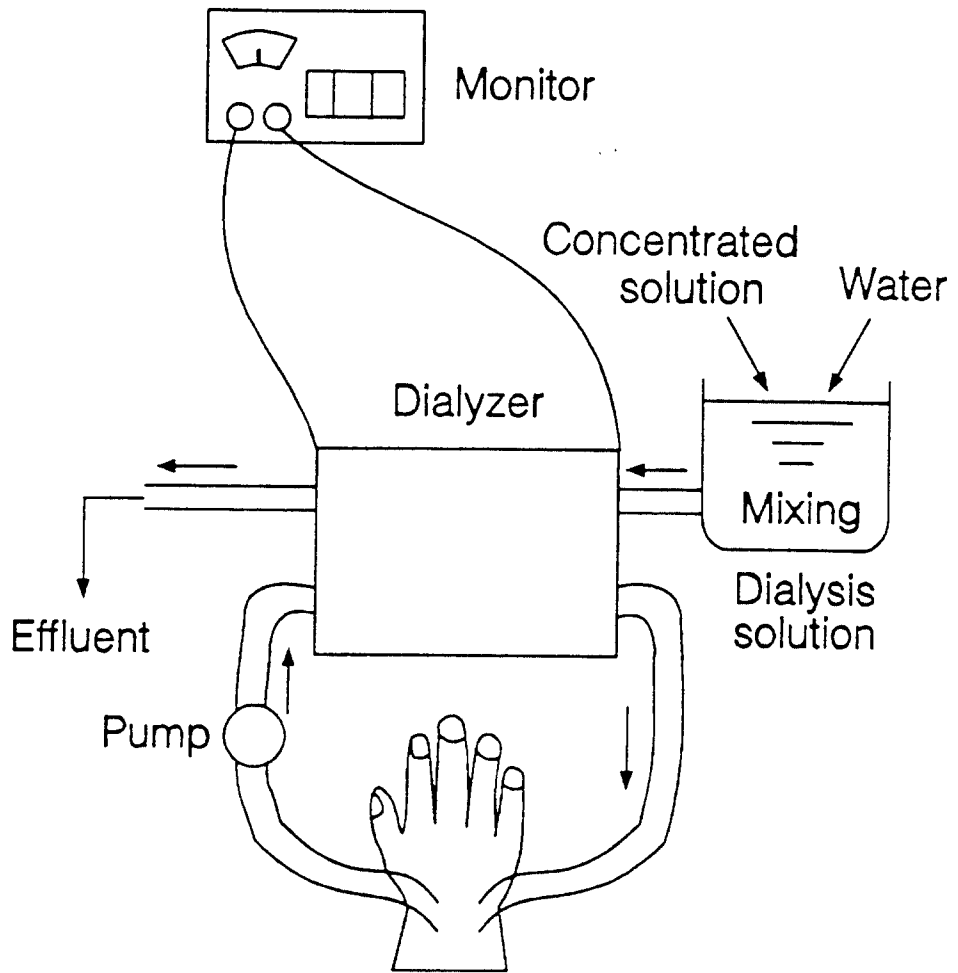
**Industrial Membrane Research Institute
Department of Chemical Engineering
University of Ottawa**

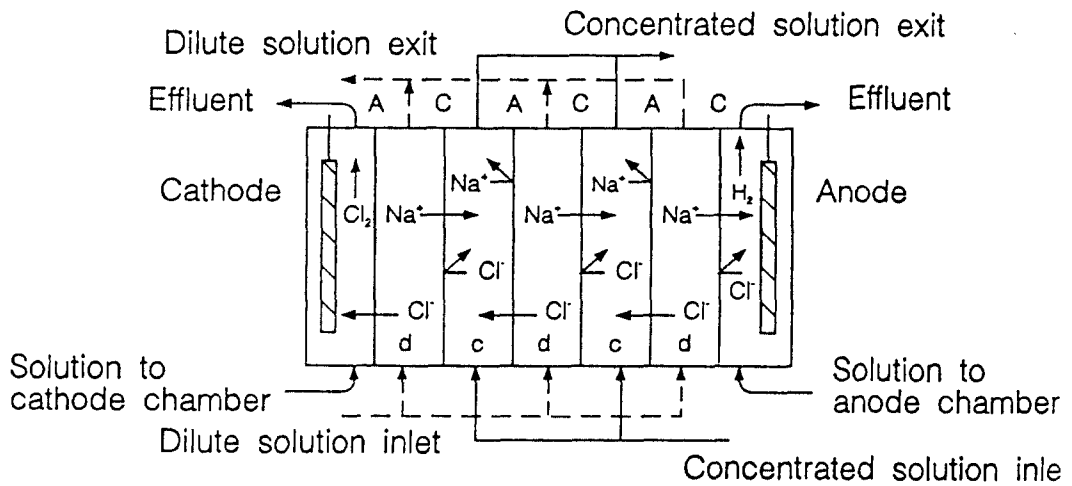
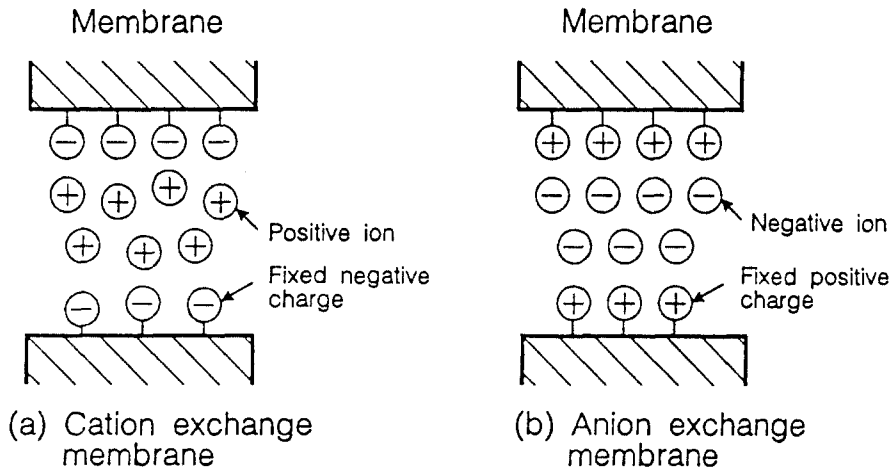
History of Membrane Process Development

Process	Year	Name
microfiltration	1920	Zsigmondy
ultrafiltration	1930	
hemodialysis	1950	Kolff
electrodialysis	1955	
reverse osmosis	1960	Loeb, Sourirajan
ultrafiltration	1960	
gas separation	1979	Henis, Tripodi
pervaporation	1982	Tusel

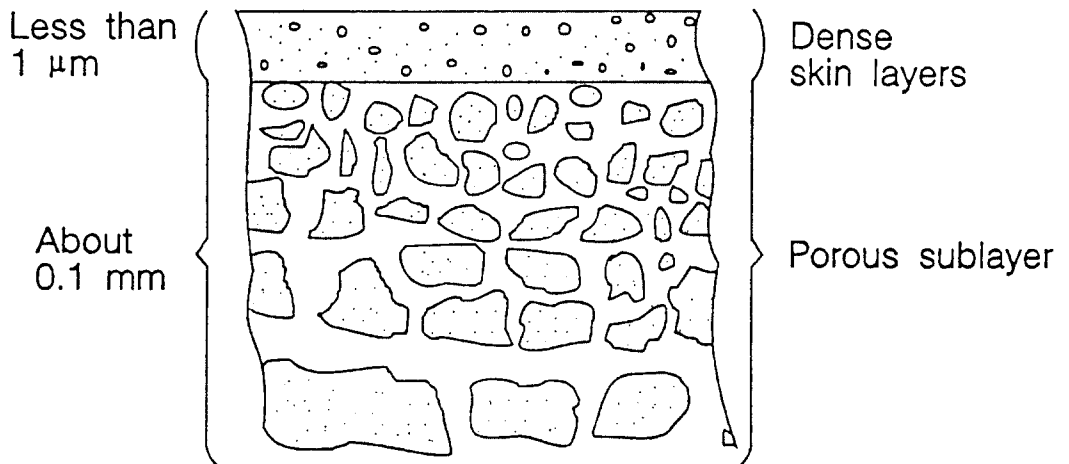
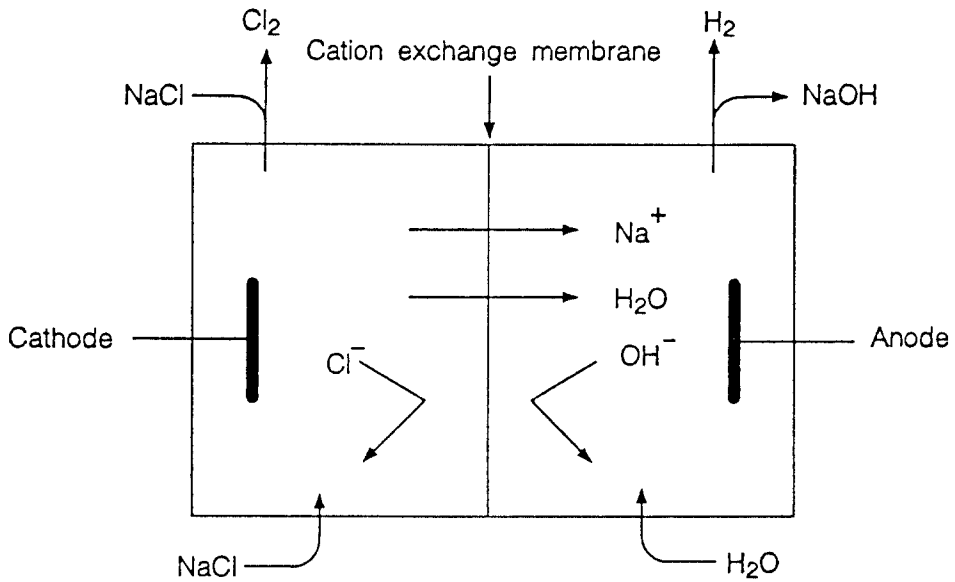


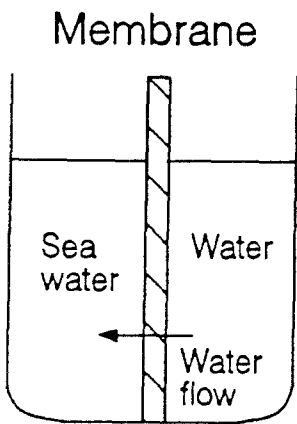




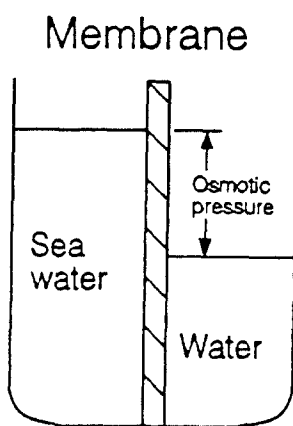


- A: anion exchange membrane
- C: cation exchange membrane
- d: dilute solution chamber
- c: concentrated solution chamber

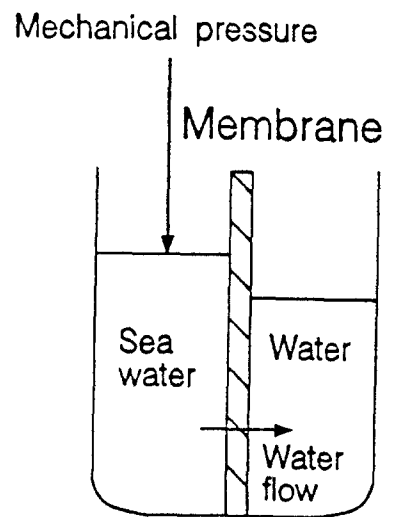




(a) Osmosis



(b) Osmotic equilibrium



(c) Reverse osmosis

Gibbs Adsorption Isotherm

Table I
Some Physicochemical Data Pertinent to Sodium Chloride Solution

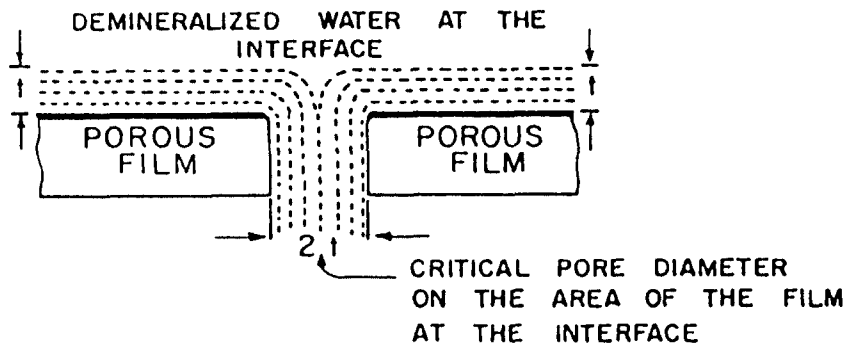
Molality (m)	Activity coefficient (α)	Density (ρ), $\times 10^{-3}$, kg/m ³	Surface tension (γ) $\times 10^3$, J/m ²
0.00	-	-	72.80
0.2010	0.751	1.00675	73.17
0.5030	0.688	1.01876	73.71
1.0204	0.650	1.0385	74.515
2.0988	0.614	1.06984	76.27
3.1920	0.714	1.1152	78.08
4.3628	0.790	1.1507	80.02
4.9730	0.848	1.1679	81.09
5.5410	0.874	1.1947	82.17

Table II
 Physicochemical Data of Sodium Chloride Solution Based on the Data
 Given in Table I

a_m , mol/kg	$\gamma \times 10^3$, J/m ²	$\frac{d\gamma}{d(a_m)} \times 10^3$	α	$\rho \times 10^{-3}$, kg/m ³	m , mol/kg	$t_1 \times 10^{10}$, m
0	72.80	2.74 ^a	1.0	1.0	0	5.62
0.5	74.16	2.70	0.669	1.024	0.747	3.78
1.0	75.50	2.52	0.624	1.056	1.603	3.35
1.5	76.68	2.15	0.616	1.081	2.435	2.87
2.0	77.65	1.82	0.640	1.103	3.125	2.57
2.5	78.50	1.67	0.685	1.122	3.650	2.54
3.0	79.32	1.62	0.745	1.139	4.027	2.68
3.5	80.12	1.58	0.795	1.152	4.403	2.82
4.0	80.90	1.49	0.833	1.164	4.802	2.79
4.5	81.61	1.35 ^b	0.861	1.179	5.226	2.64

a. Calculated as $-3 \times 72.80 + 4 \times 74.16 - 75.50 = 2.74$

b. Calculated as $80.12 - 4 \times 80.9 + 3 \times 81.61 = 1.35$



Module Development

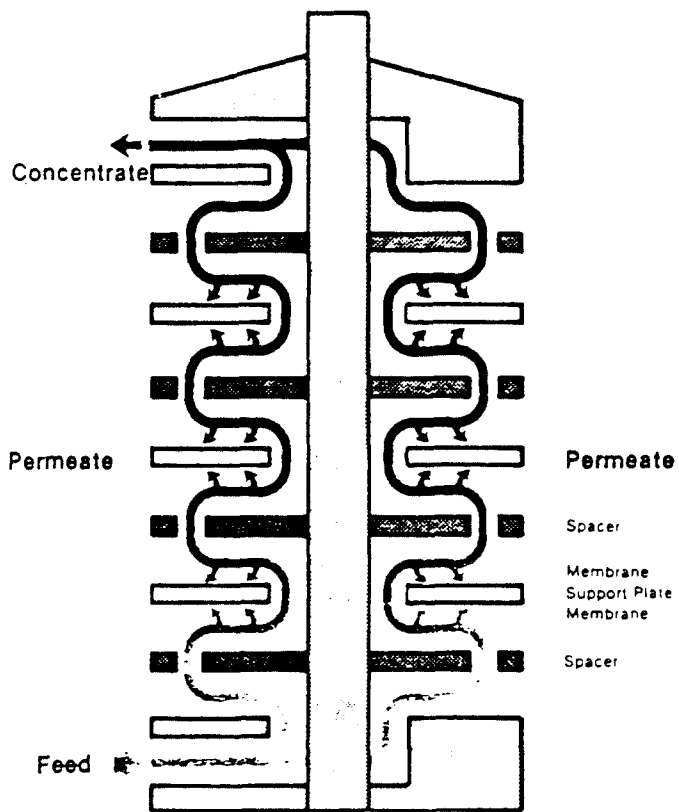
> Plate and Frame

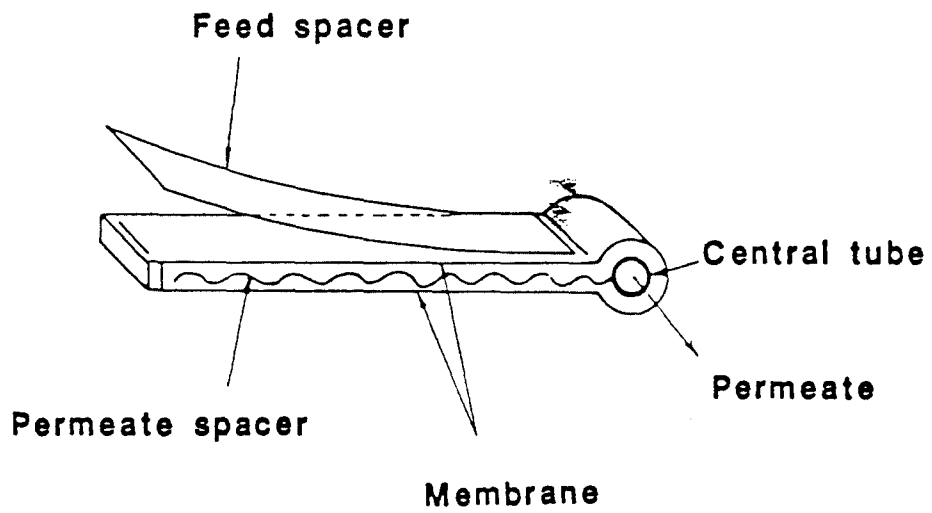
> Spiral Wound

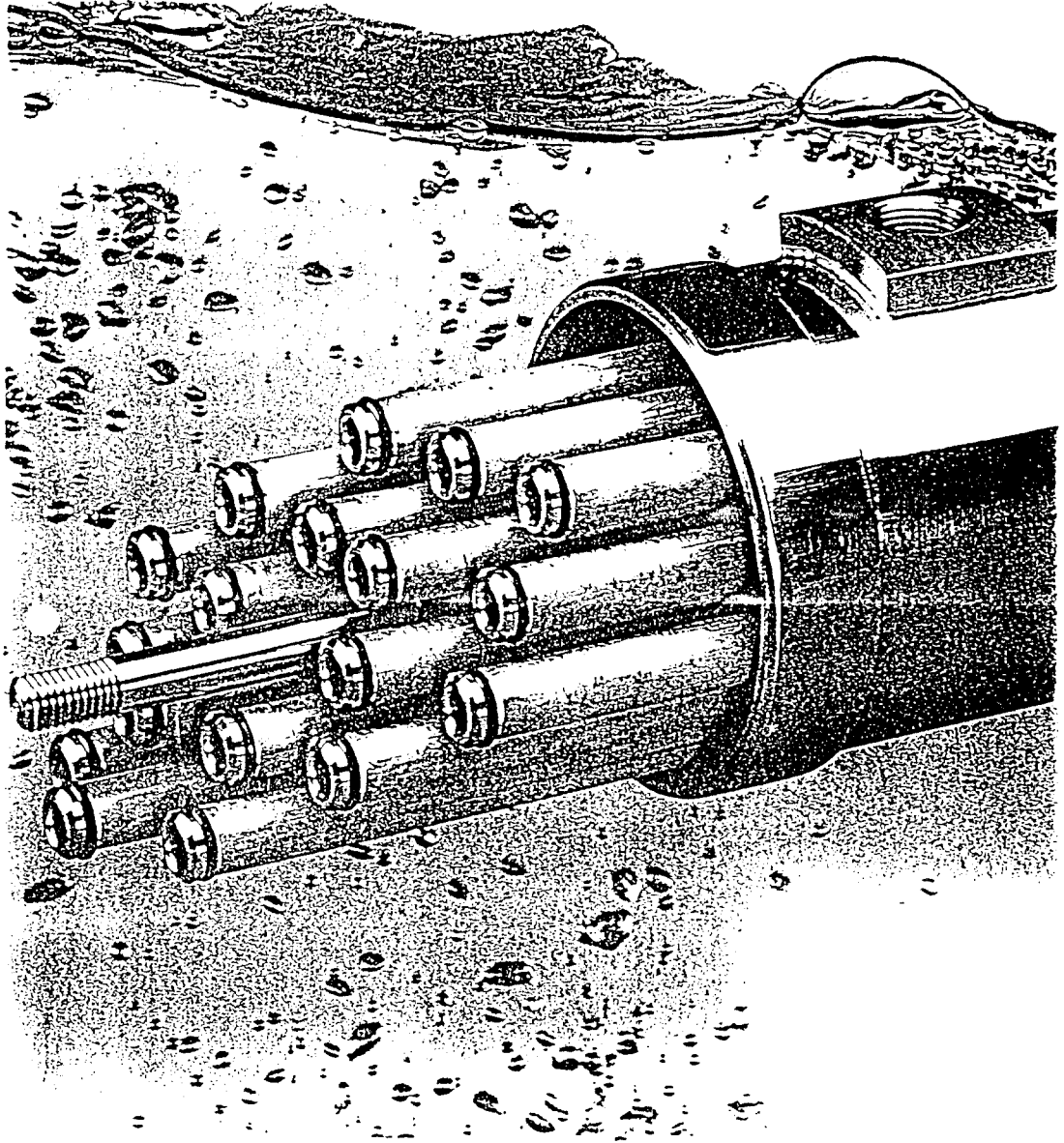
> Tubular

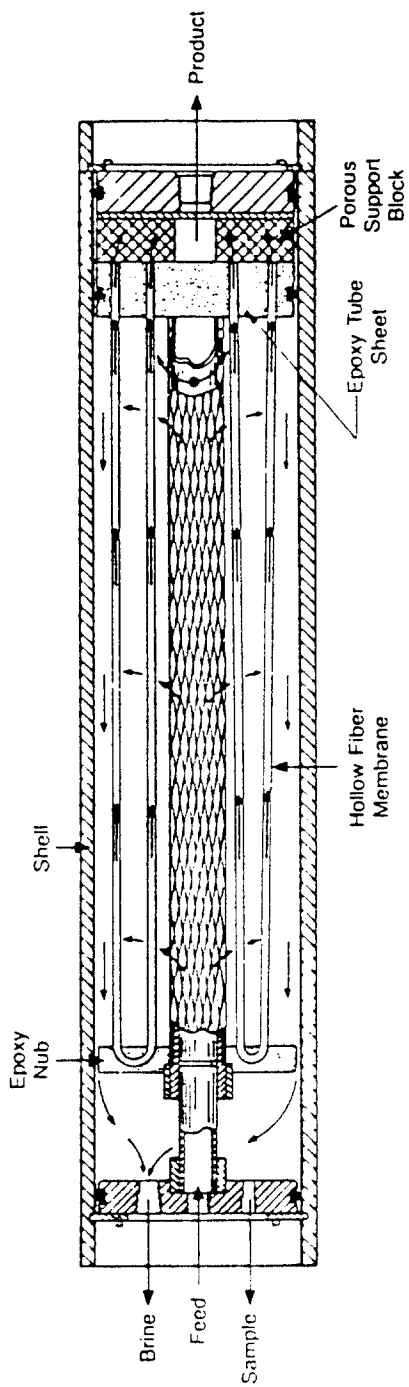
> Hollow Fiber

Internal Flow







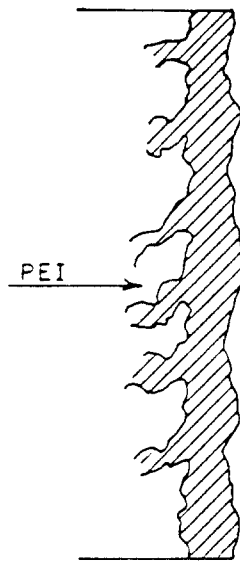


Development of Composite Membrane

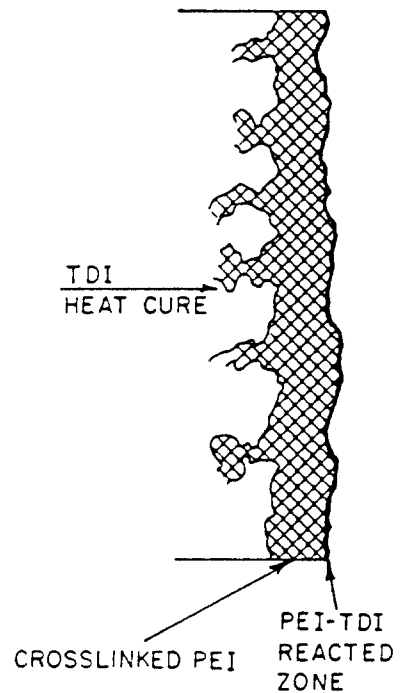
> In-situ Polymerization



SURFACE OF
POLYSULFONE
SUPPORT FILM



PEI COATING



Improvement in the Separation of Organic Solutes

Cellulose acetate membrane with NaCl separation of 96.7 %

Solute	$k \times 10^4$ cm/s	Seprn. %	Solute	$k \times 10^4$ cm/s	Seprn. %
NaF	18.3	98.0	Sr(NO ₃) ₂	17.3	96.4
NaHCOO	18.2	97.7	Th(NO ₃) ₄	11.1	99.9
NaHCO ₃	16.9	98.6	Zn(NO ₃) ₂	16.5	96.3
NaH phthalate	17.9	97.3	ZnSO ₄	* 13.0	>99.9
NaH ₂ PO ₄	16.3	99.4	<u>Alcohols</u>		
NaHSO ₄	17.8	99.4	Methanol	22.6	9.4
Na hydroxy-benzoate	15.0	98.9	Ethanol	18.7	18.2
NaI	20.0	95.2	1-Propanol	16.5	29.3
NaIO ₃	16.4	99.0	2-Propanol	16.5	48.0
Na ₃ Fe(CN) ₆	* 16.3	>99.9	1-Butanol	15.0	21.8
Na ₄ Fe(CN) ₆	* 16.0	>99.9	2-Butanol	15.0	49.7
Na isobutyrate	15.4	99.3	2-Methyl-1-propanol	15.0	49.7
Na m-nitrobenzoate	15.0	99.2	2-Methyl-2-propanol	15.0	86.8
Na o-nitrobenzoate	15.0	99.6	1-Pentanol	13.9	18.5
Na p-nitrobenzoate	15.0	99.2	2-Pentanol	13.9	51.7
NaNO ₂	18.5	94.4	3-Pentanol	13.9	51.7
NaNO ₃	19.6	93.5	2-Methyl-1-butanol	13.9	51.7
NaOH	15.1	99.4	3-Methyl-1-butanol	13.9	51.7
Na phenylacetate	14.6	98.9	2,2-Dimethyl-1-propanol	13.9	75.7
Na 4-phenylbutyrate	13.2	99.1	1-Hexanol	13.0	15.5
Na β-phenylpropionate	13.5	99.1	2-Hexanol	13.0	29.2
Na pivalate	14.9	99.7	3-Hexanol	13.0	29.2
Na propionate	15.5	99.3	2-Methyl-1-pentanol	13.0	29.2
Na ₂ SO ₃	16.6	99.8	3-Methyl-1-pentanol	13.0	29.2
Na ₂ SO ₄	16.7	99.8	4-Methyl-1-pentanol	13.0	29.2
Na ₂ S ₂ O ₃	17.1	>99.9	3-Methyl-2-pentanol	13.0	53.1
Na toluate	12.0	98.8	2-Methyl-3-pentanol	13.0	53.1
Na valerate	15.2	99.3			

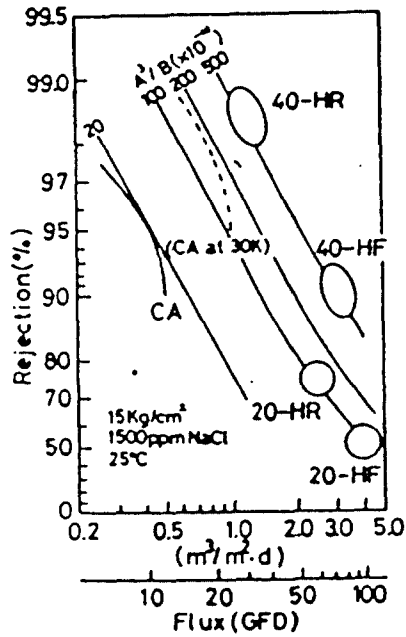
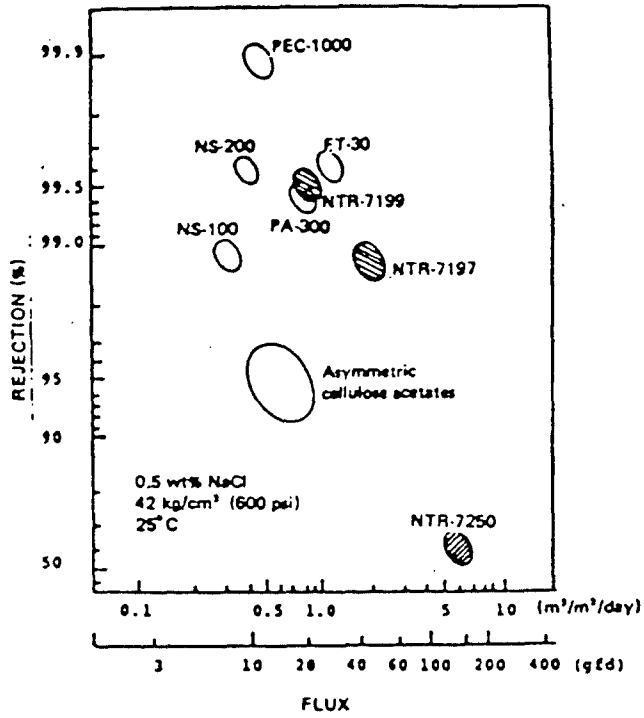
Table 33. Reverse Osmosis Separation Characteristics of
PEC-1000 Membranes at 800 psig and 25 °C^[291]

Solute	Solute concn. in feed, wt-%	pH	Solute rejection, %	Water flux, m ³ /m ² day
Methyl alcohol	5	6.9	41	0.38
Ethyl alcohol	5	5.0	92	0.30
Isopropyl alcohol	5	6.5	99.5	0.32
n-Butyl alcohol	5	5.6	99	0.30
Benzyl alcohol	4	7.0	82	0.10
Ethylene glycol	5	6.8	94	0.36
Propylene glycol	5	5.8	99.7	0.40
Glycerine	5	5.8	99.9	0.43
Phenol	1	5.2	99.0	0.24
Formic acid	5	1.9	34	0.52
Acetic acid	5	2.6	91	0.37
Propionic acid	5	2.7	97	0.39
Oxalic acid	0.5	1.8	99.1	0.69
Formaldehyde	5	3.6	69	0.30
Acetaldehyde	3	3.6	89	0.46
Acetone	4	6.7	97	0.29
Methyl ethyl ketone	4	6.6	98	0.21
Ethyl acetate	4	6.8	99.2	0.18
n-Butyl acetate	1	6.9	99.6	0.38
Tetrahydrofuran	5	6.7	99.8	0.28
1,4-Dioxane	5	6.6	99.9	0.40
Ethyldiamine	5	12.1	99.5	0.08
Aniline	1	8.3	95	0.11
Urea	1	6.9	85	0.56
N,N-Dimethylformamide	5	6.5	98	0.32
N,N-Dimethylacetamide	5	6.5	99.6	0.30
ε-Caprolactam	5	5.8	99.9	0.30
Dimethylsulfoxide	5	6.4	99.6	0.34
Lactose	5	6.1	>99.9	0.50

Table 32. Reverse Osmosis Separation Characteristics of
PA-300 Membranes at 1000 μ sig and 25°C^[290]

Solute	Solute conc., ppm	pH	Solute rejection, %
Sodium nitrate	10,000	6.0	99.0
Ammonium nitrate	9,600	5.7	98.1
Boric acid	280	4.8	65 - 70
Urea	1,250	4.9	80 - 85
Phenol	100	4.9	93
Phenol	100	12.0	> 99
Ethyl alcohol	700	4.7	90
Glycerine	1,400	5.6	99.7
DL-aspartic acid	1,500	3.2	98.3
Ethyl acetate	366	6.0	95.3
Methyl ethyl ketone	465	5.2	94
Acetic acid	190	3.8	65-70
Acetonitrile	425	6.3	> 25
Acetaldehyde	660	5.8	70-75
Dimethyl phthalate	37	6.2	> 95
2,4-Dichlorophenoxy acetic acid	130	3.3	> 98.5
Citric acid	10,000	2.6	99.9
Alcozyme (soap)	2,000	9.3	99.3
o-Phenyl phenol	110	6.5	> 99
Tetrachloroethylene	104	5.9	> 93
Sodium silicate	42	8.6	> 96
Sodium chromate	1,200	7.8	> 99
Chromic acid	870	3.9	90-95
Cupric chloride	1,000	5.0	99.2
Zinc chloride	1,000	5.2	99.3
Trichlorobenzene	100	6.2	> 99
Butyl benzoate	200	5.8	99.3

Improvement in Reverse Osmosis Membrane Flux



Membrane Gas Separation

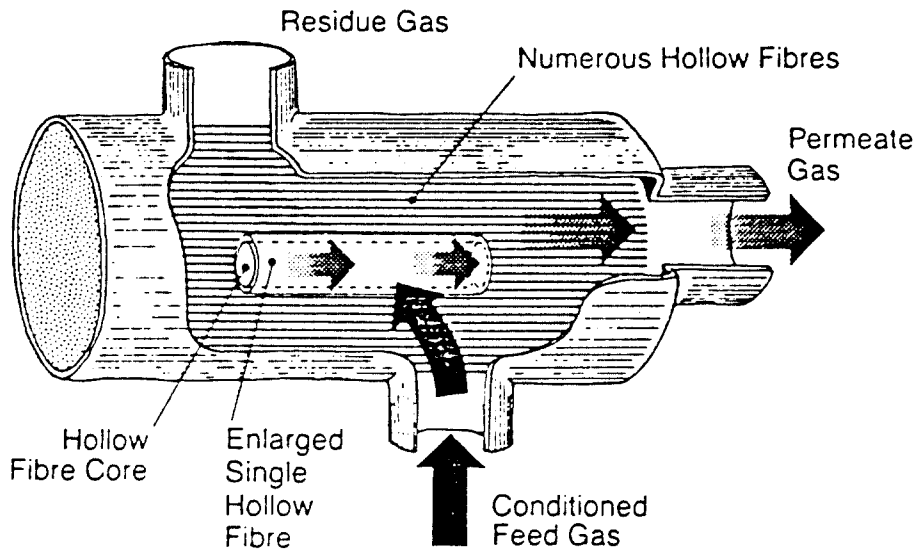
> Dry Asymmetric Membranes

**Hollow Fiber, Spiral Wound
Cellulose Acetate, Polyamide, Polyimide**

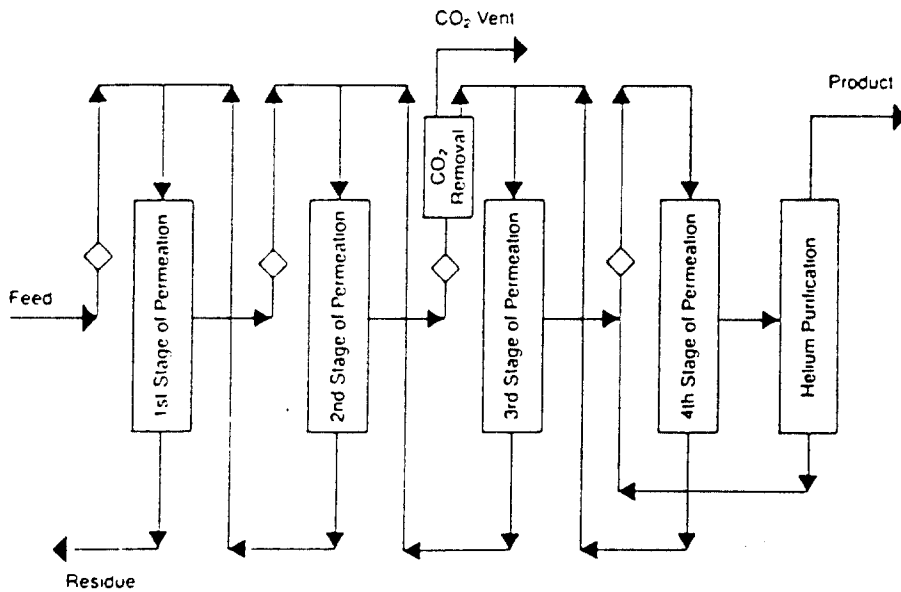
> Composite Membranes

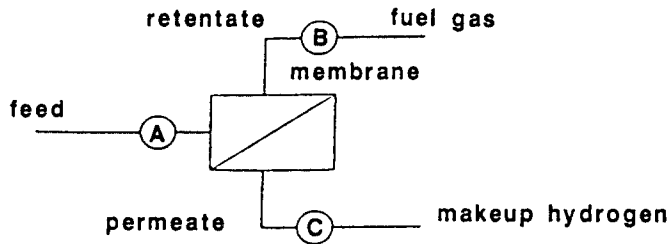
PRISM Membrane, PRISM Alpha Membrane

Resistance Theory



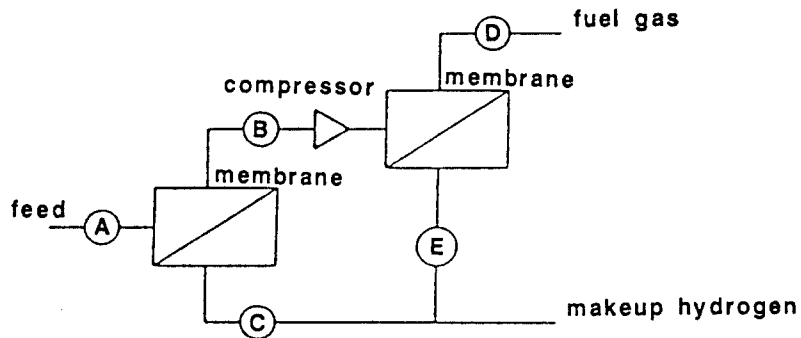
(Source: International Permeator Inc. 1966)





	A	B	C
Composition (mole %)			
H ₂	71.0 (55.0)	26.3 (41.7)	98.0 (98.0)
CH ₄	16.0 (18.9)	40.3 (24.4)	1.3 (1.1)
C ₂ ⁺	13.0 (26.1)	33.4 (33.9)	0.7 (0.9)
Flow rate (Nm ³ /day)	1000 (1000)	377 (764)	623 (236)
Pressure (bar)	30.0	30.0	5.0
H ₂ recovery: 86.0% (42.1%)			
α (H ₂ /CH ₄) = 60			

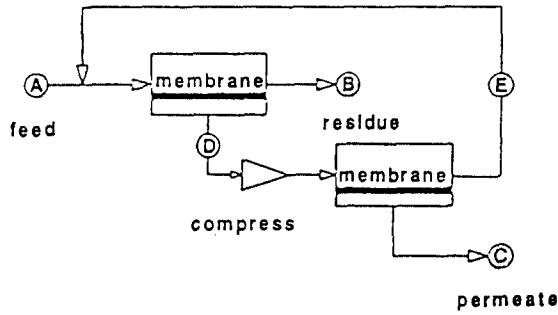
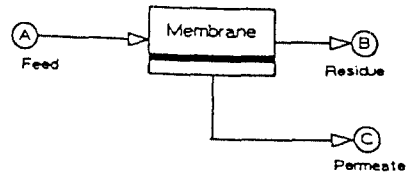
* figures in brackets illustrate the effect of lower feed purity



	A	B	C	D	E
Composition (mole %)					
H ₂	55.0	41.7	98.0	18.8	96.0
CH ₄	18.9	24.4	1.1	33.7	2.2
C ₂ ⁺	26.1	33.9	0.9	47.5	1.8
Flow rate (Nm ³ /day)	1000	764	236	538	226
Pressure (bar)	30.0	30.0	5.0	60.0	5.0
H ₂ recovery: 81.5%					

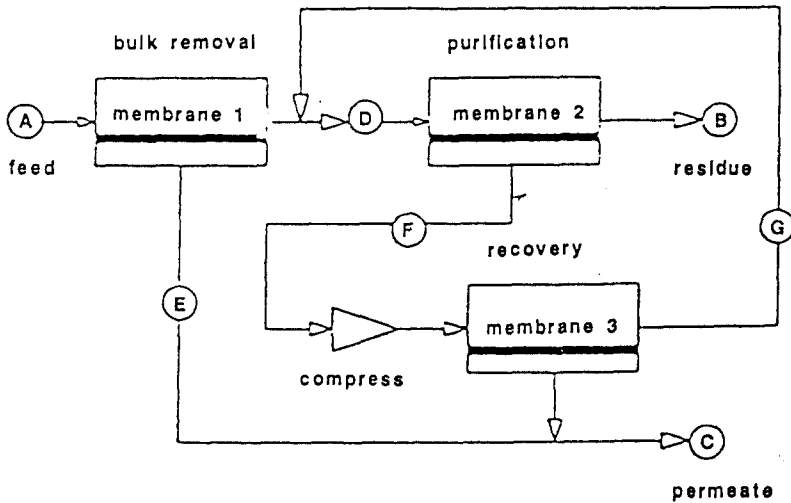
	A	B	C
Composition (mole%)			
CH ₄	93.0	98.0	63.4
CO ₂	7.0	2.0	36.6
Flow rate (MM _{SCFD})	20.00	17.11	2.89
Pressure (psig)	850	835	10

Methane Recovery = 92%



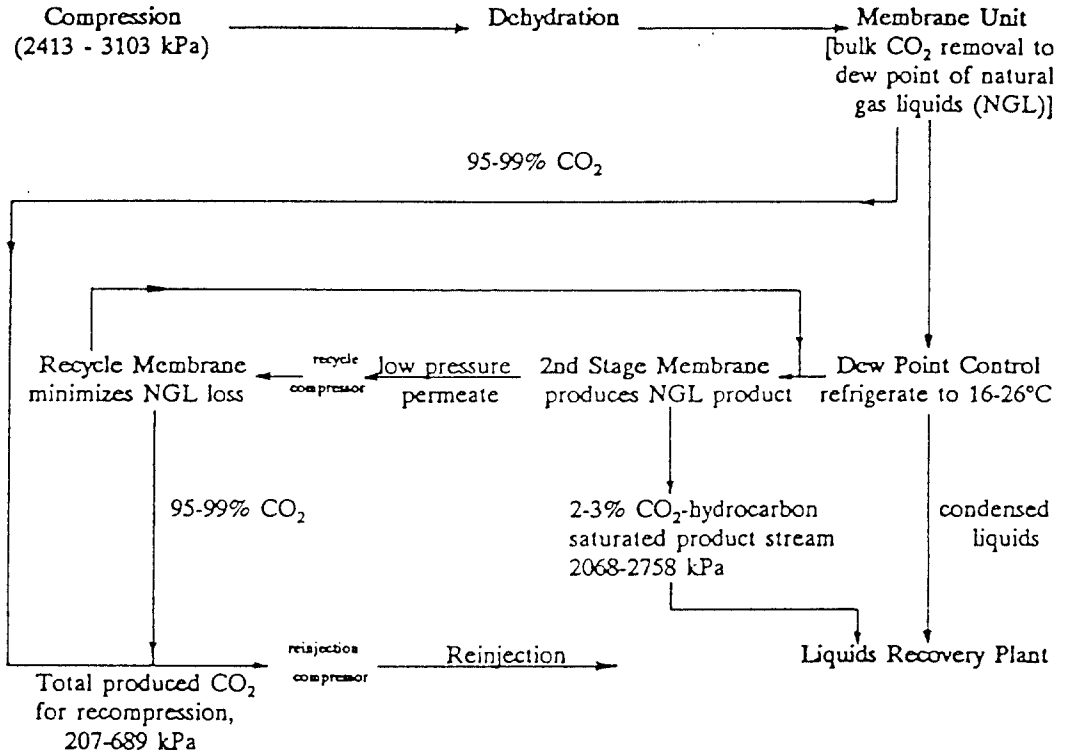
	A	B	C	D	E
Composition (mole %)					
CH ₄	93.0	98.0	18.9	63.4	93.0
CO ₂	7.0	2.0	81.1	36.6	7.0
Flow Rate (MM _{SCFD})	20.00	18.74	1.26	3.16	1.90
Pressure (psig)	850	835	10	10	850

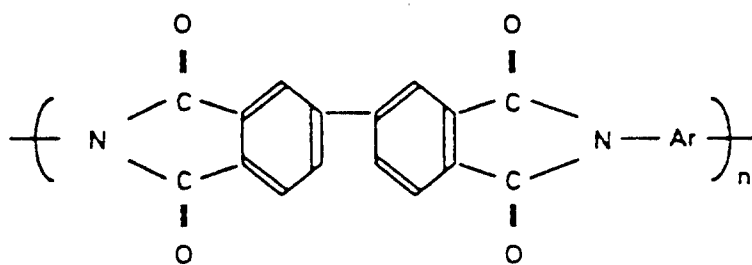
Methane Recovery = 98.7%



	A	B	C	D	E	F	G
Composition (mole%)							
CH ₄	93.0	98.0	49.2	96.1	56.1	72.1	93.0
CO ₂	7.0	2.0	50.8	3.9	43.9	27.9	7.0
Flow Rate (MM _{SCFD})	20.00	17.95	2.05	19.39	1.62	1.44	1.01
Pressure (psig)	850	835	10	840	10	10	850

Methane Recovery = 94.6%

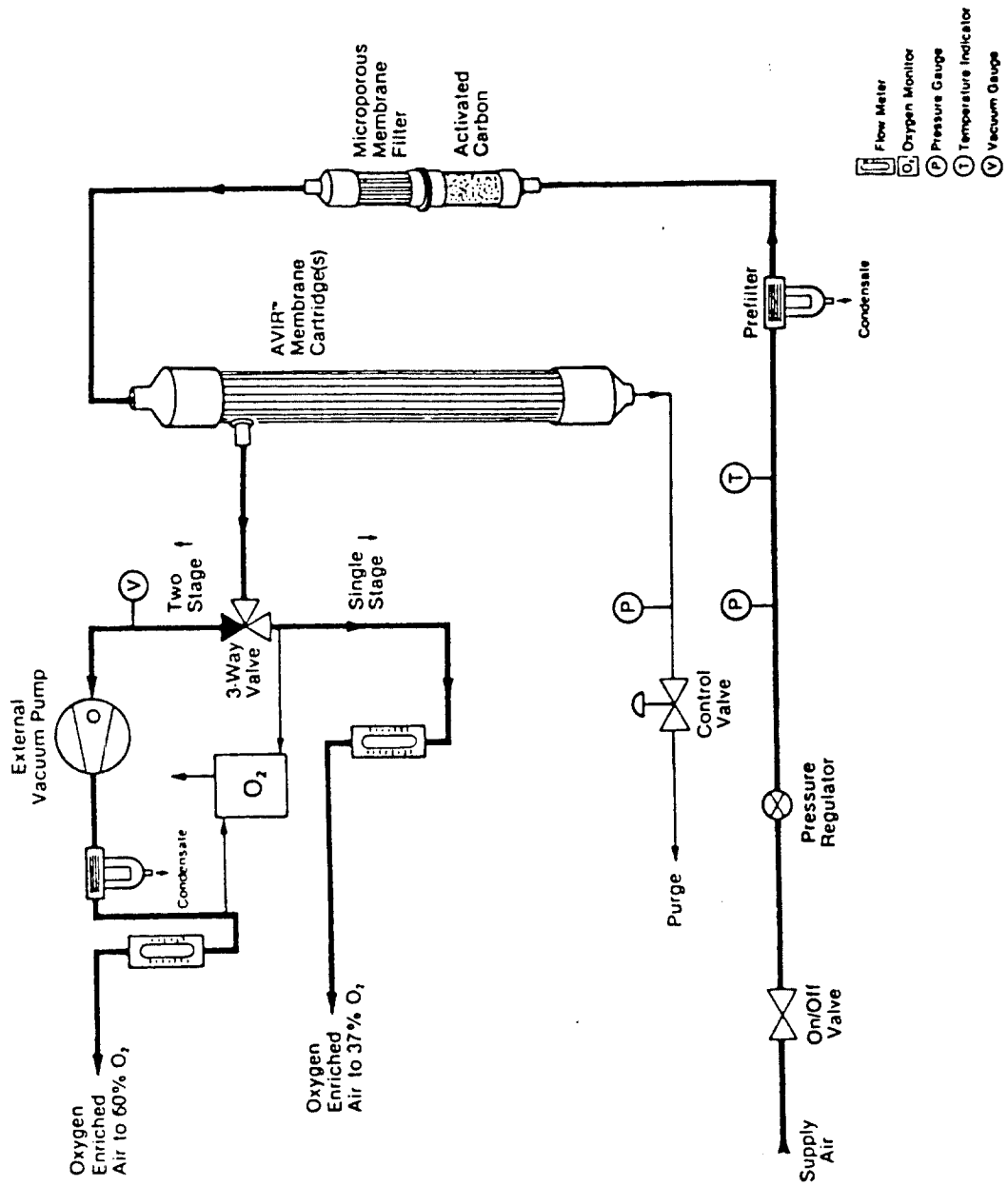




Ar shows divalent aromatic radical

Example permeability data for UBE's polyimide membranes

Membrane Type	A (60degC) (140degF)	B-H (60degC) (140degF)	C (30degC) (86degF)	D (120degC) (248degF)
Permeation rate [STP • cc/cm ² • sec • cmHg]		H ₂ O	H ₂ O	H ₂ O
	10 ⁻³			
		H ₂	CO ₂	H ₂
		He	He	
	10 ⁻⁴			
		H ₂ S	CO ₂	CH ₃ OH
		O ₂		
	10 ⁻⁵			
		CO ₂	Ar	O ₂
			CO	EtOH
			N ₂	
		H ₂ S	CH ₄	
		O ₂		Ar
	10 ⁻⁶			
		Ar		N ₂
		CO	C ₃ H ₆	
			C ₂ H ₆	
		N ₂		
		C ₂ H ₄		
		CH ₄		PrOH
10 ⁻⁷				
	C ₂ H ₆	C ₃ H ₈	EtAc	



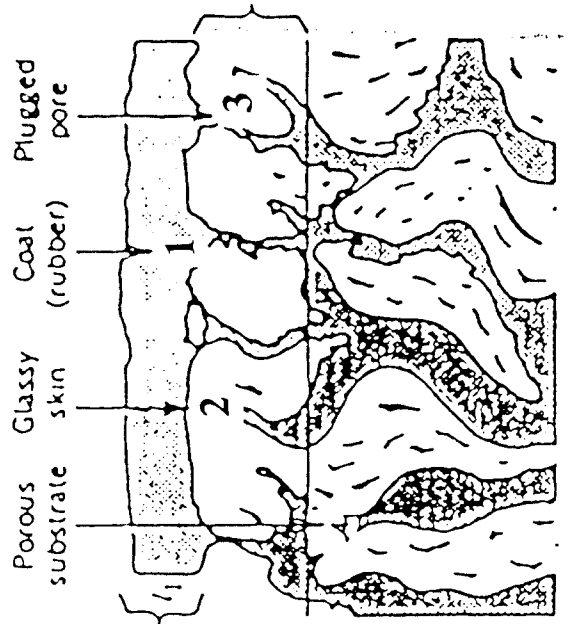
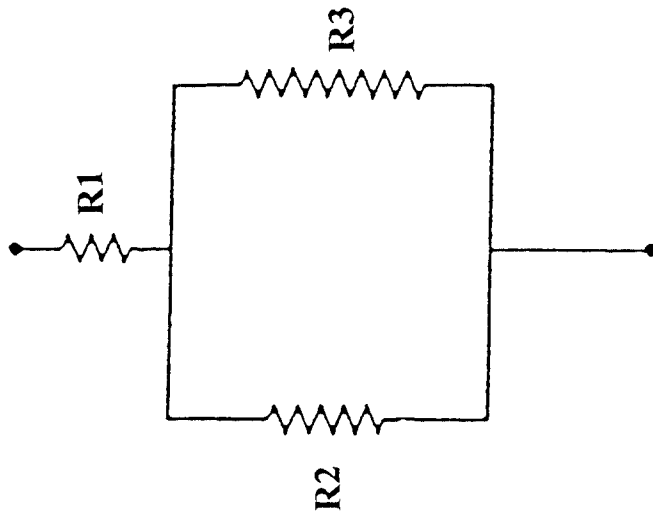
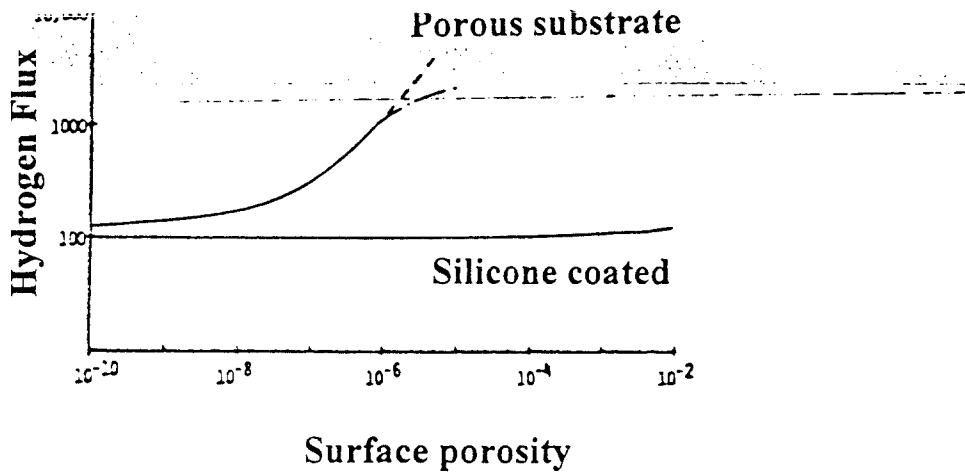
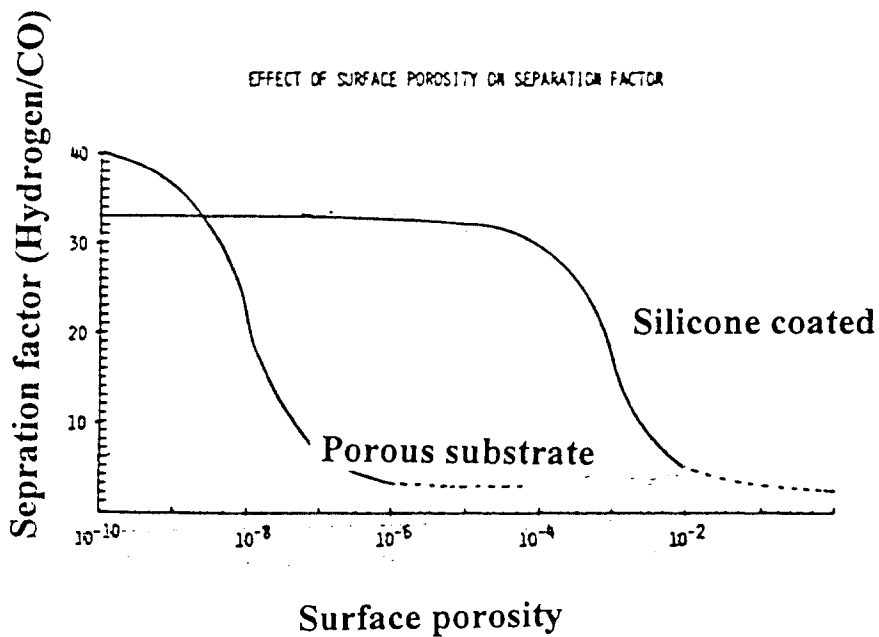


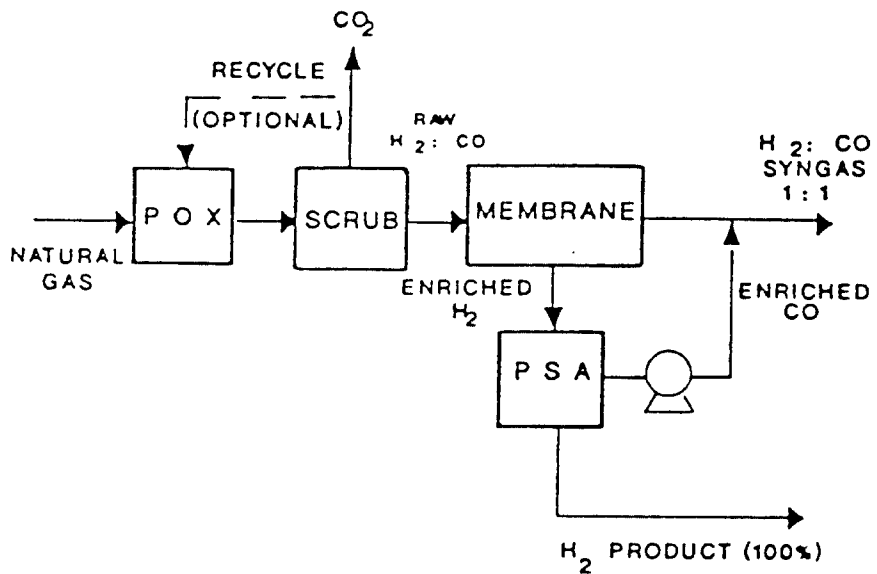
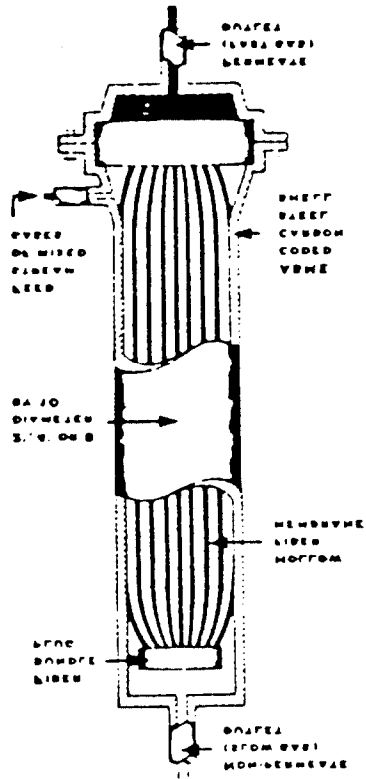
Figure 3: Coated membrane and electric circuit analog.

EFFECT OF SURFACE POROSITY ON H_2 FLUX



EFFECT OF SURFACE POROSITY ON SEPARATION FACTOR





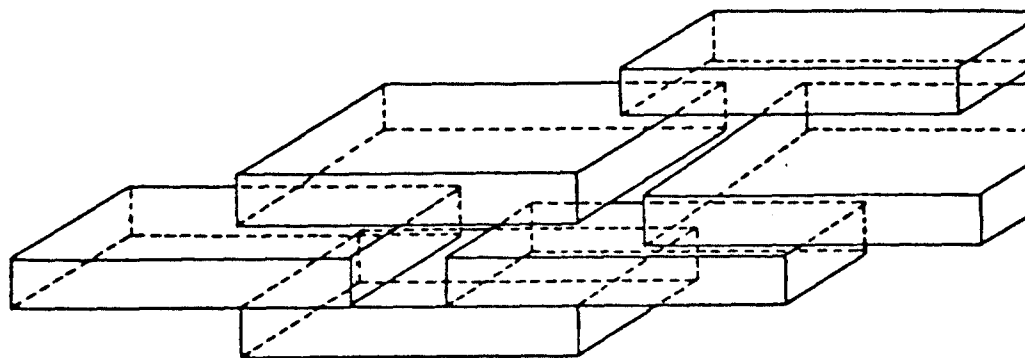
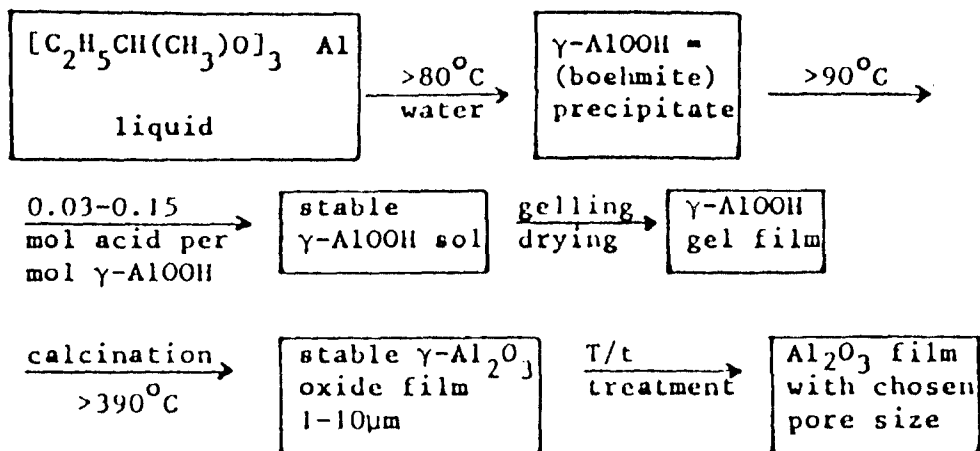
Development of Inorganic Membranes

> Alumina Membrane

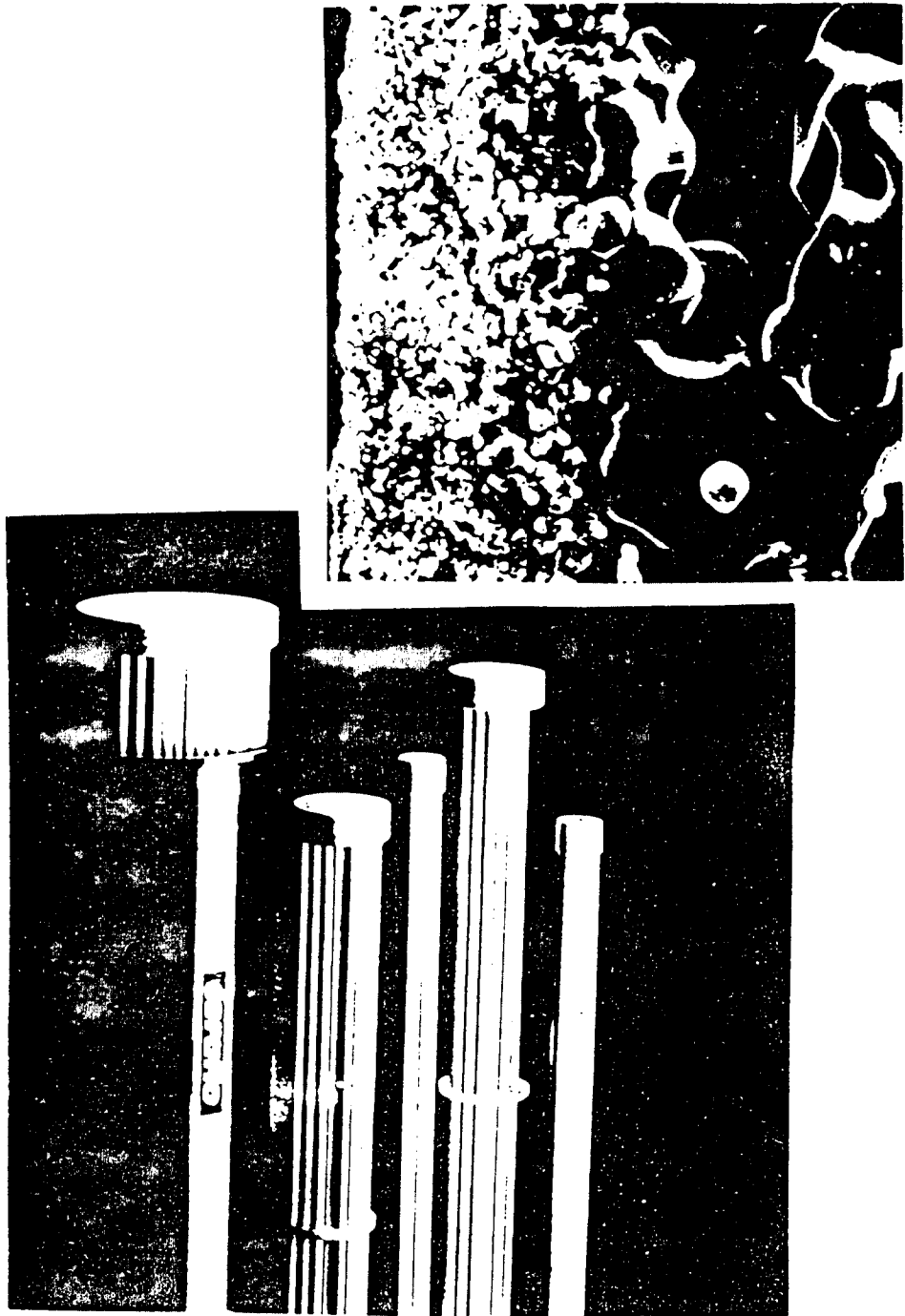
Sol-Gel Method

> Porous Carbon Membrane

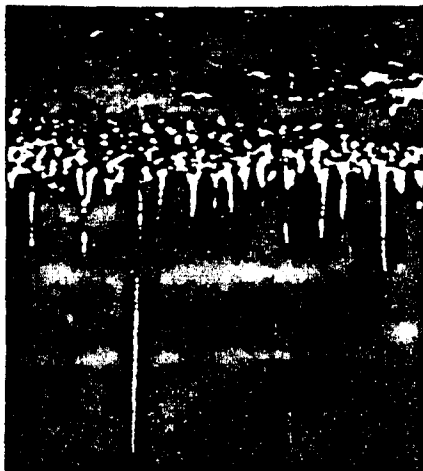
> Zeolite Membrane



Model of boehmite membrane microstructure



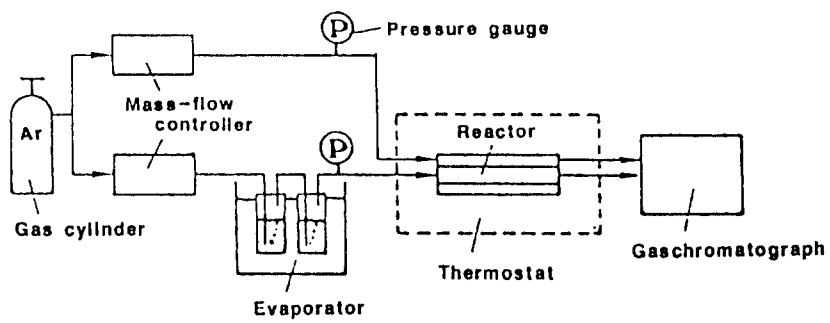
5. Asymmetric structure of Ceraflo membrane (a), and tube assembly (b) (13).

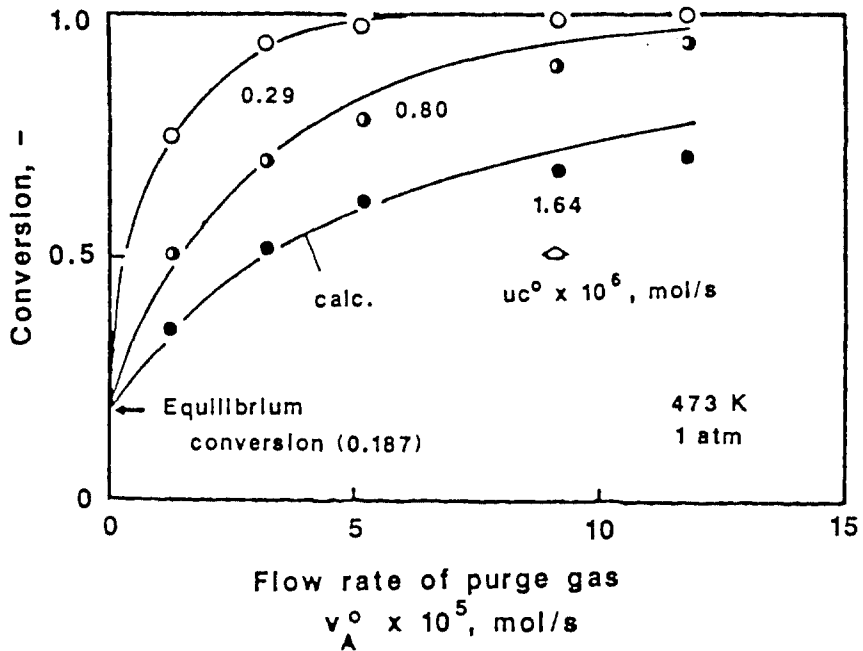
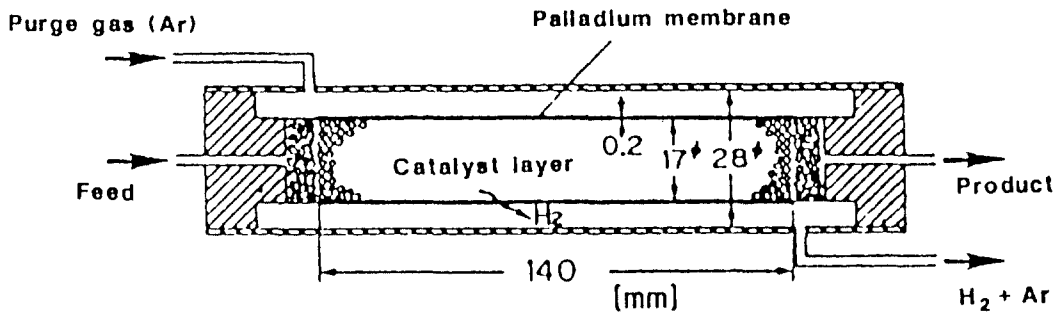


4. Surface retention of particles by Anotech ANOPORE Membrane.

Membrane Reactor

> Shift in Equilibrium

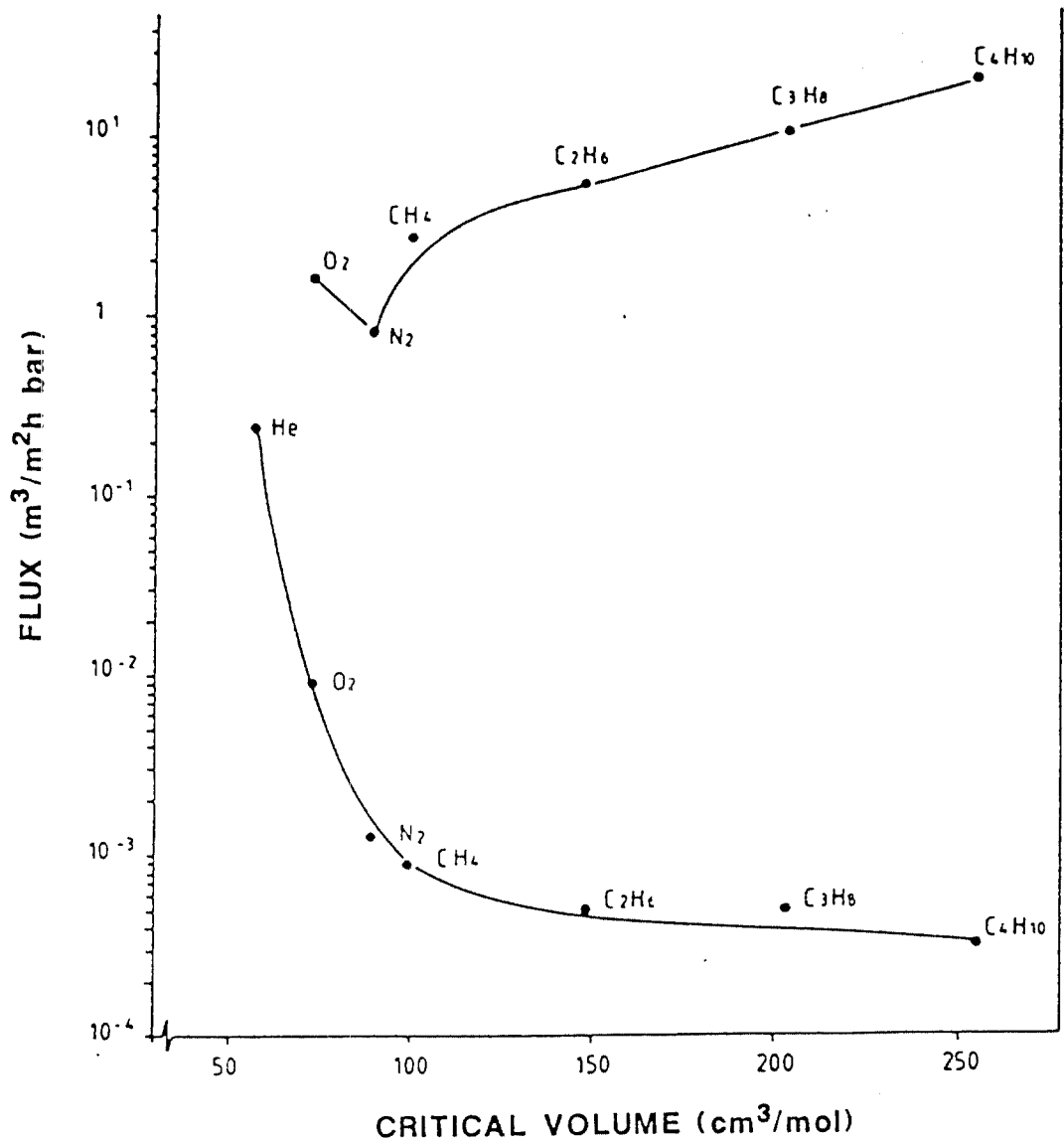


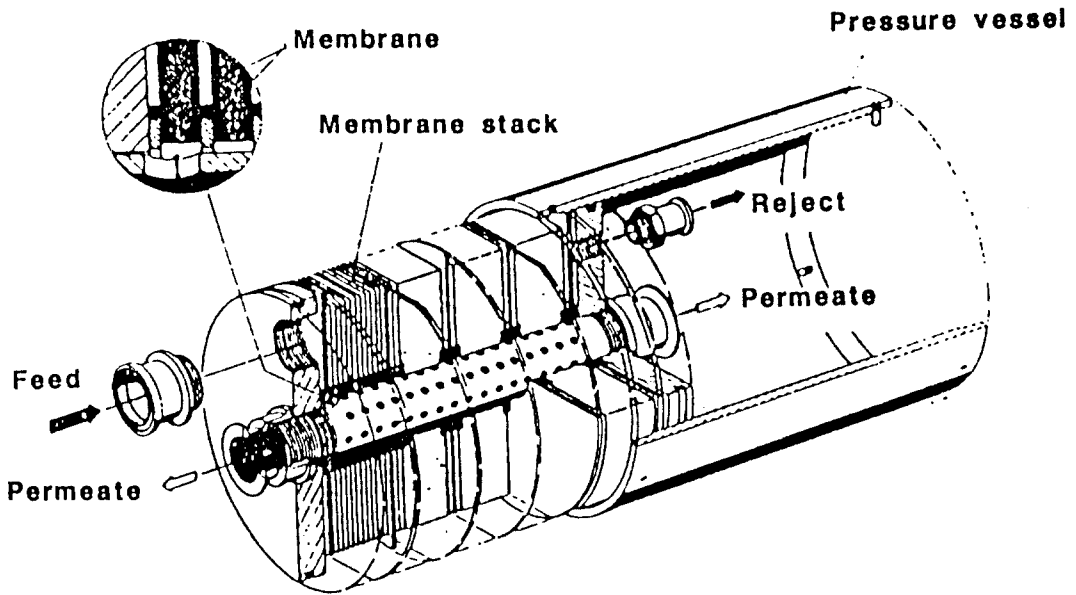
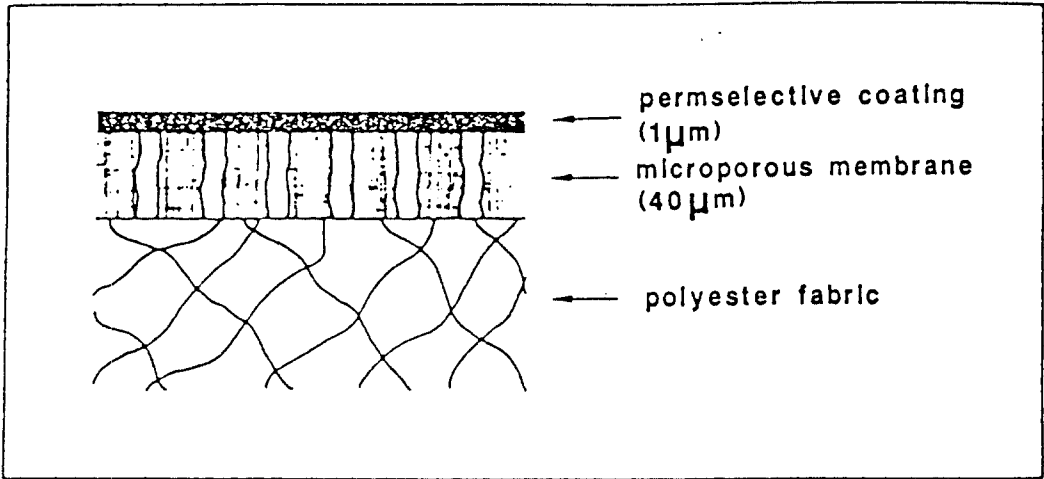


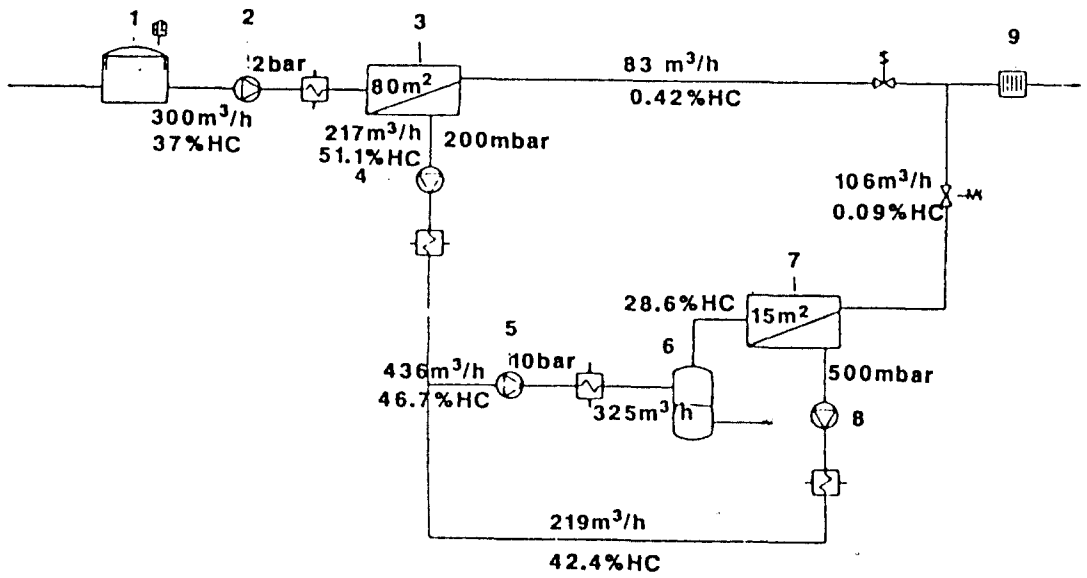
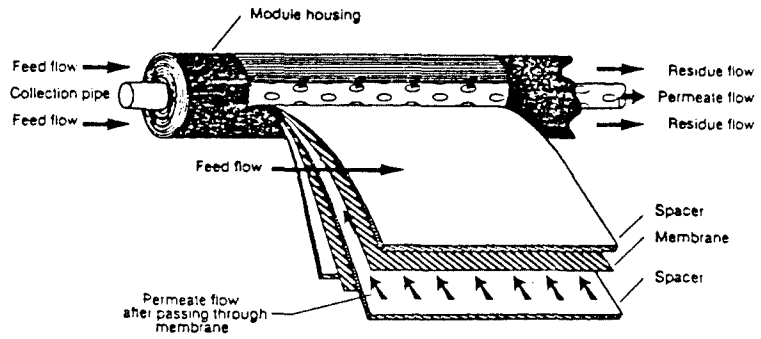
Vapor Permeation

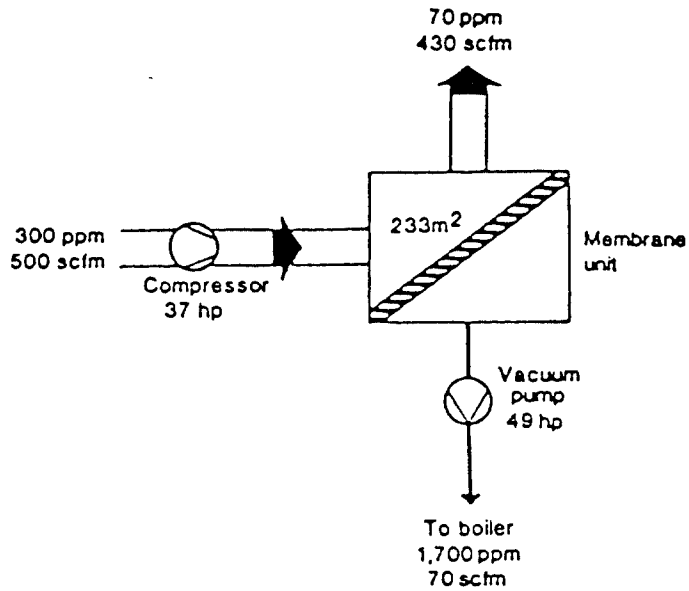
> VOC Removal from Air

> Dehumidification

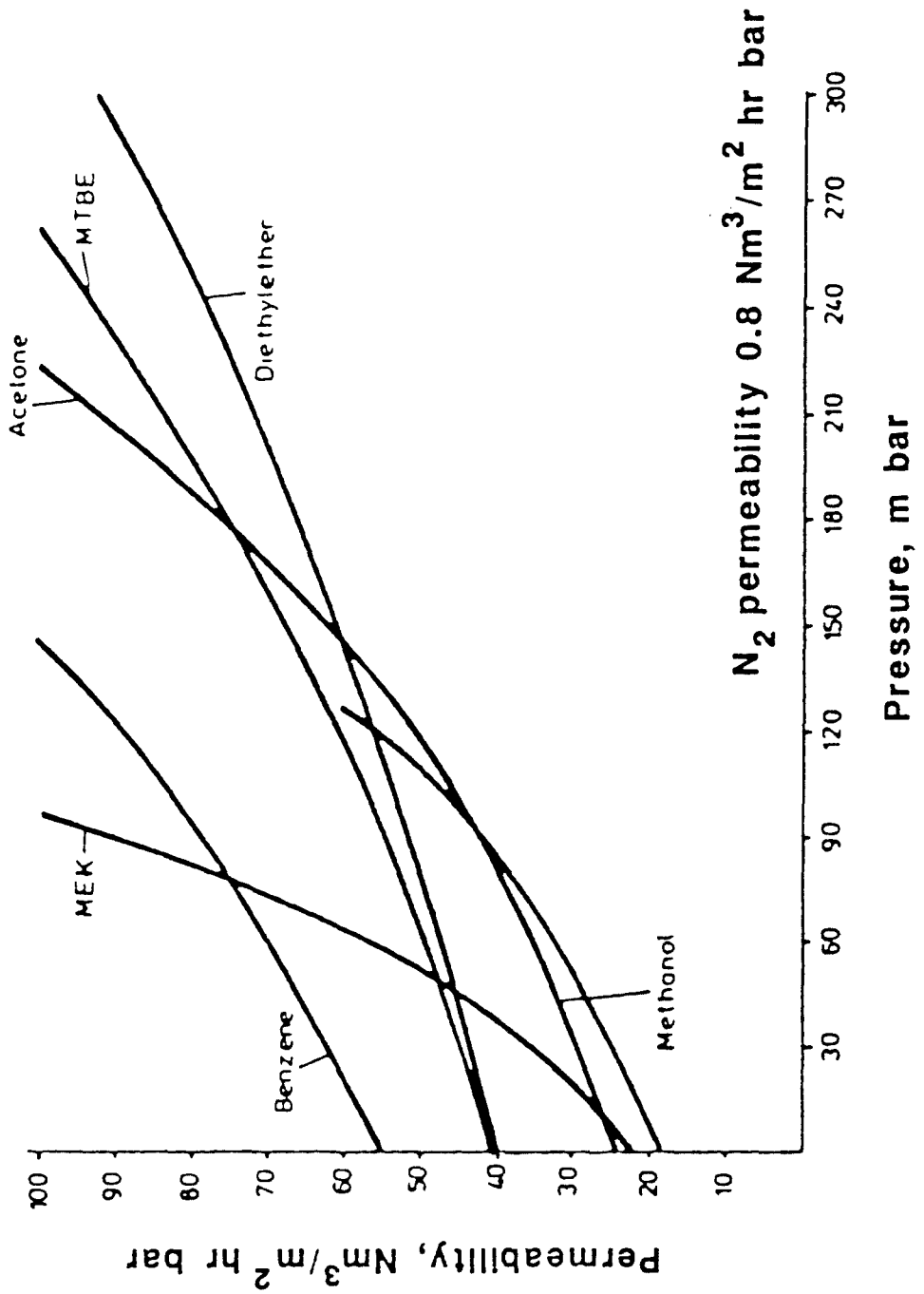




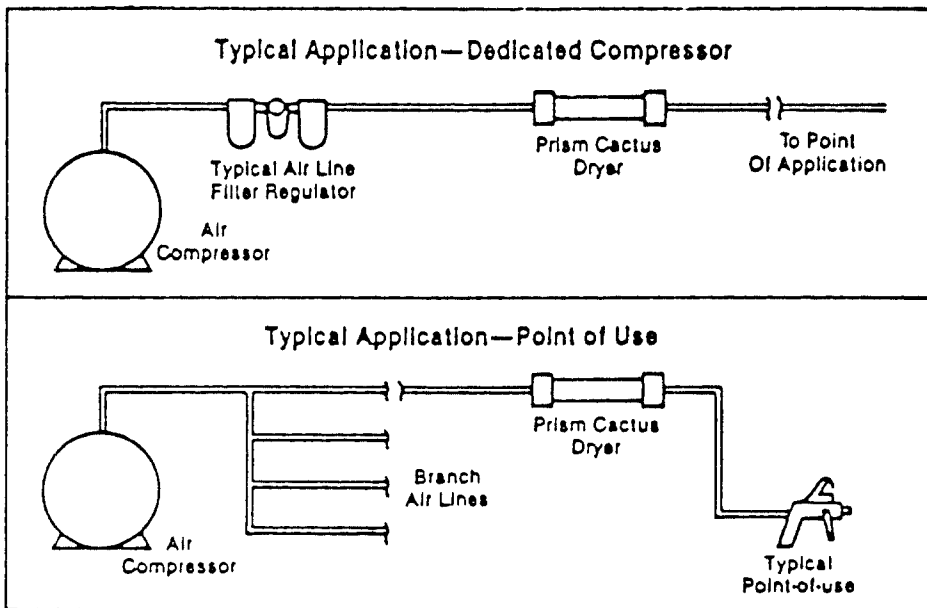
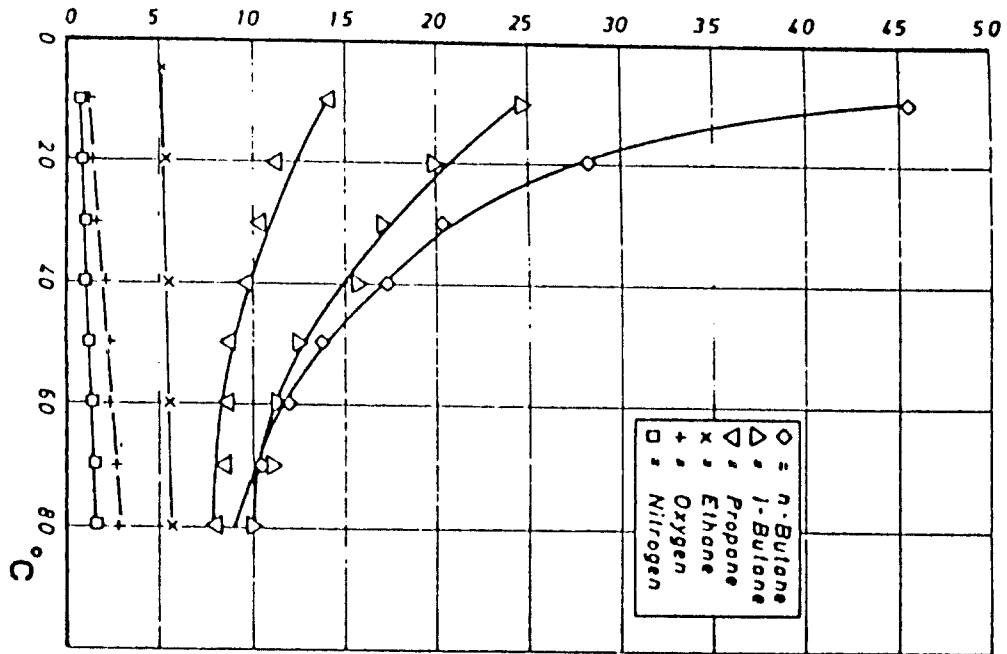




	<u>FEED</u>	<u>PERMEATE</u>	<u>RESIDUE</u>
Flow (scfm)	500	70	430
Concentration (ppm)	300	1,700	70
Membrane Selectivity		30	
Membrane Area		233 m ²	
Vacuum Pumps		49 hp	
Compressors		37 hp	
CAPITAL COSTS		\$282,000	
		\$560/scfm feed	
OPERATING COSTS			
Depreciation + Interest		\$ 33,200	
Miscellaneous		10,400	
Module replacement (3-year lifetime)		46,600	
Energy		22,800	
		<hr/>	
		\$113,000/yr	
OPERATING COST		\$0.52/1000 scf feed	
		0.68/lb solvent recovered	



Flux Density, Nm³/m² h bar

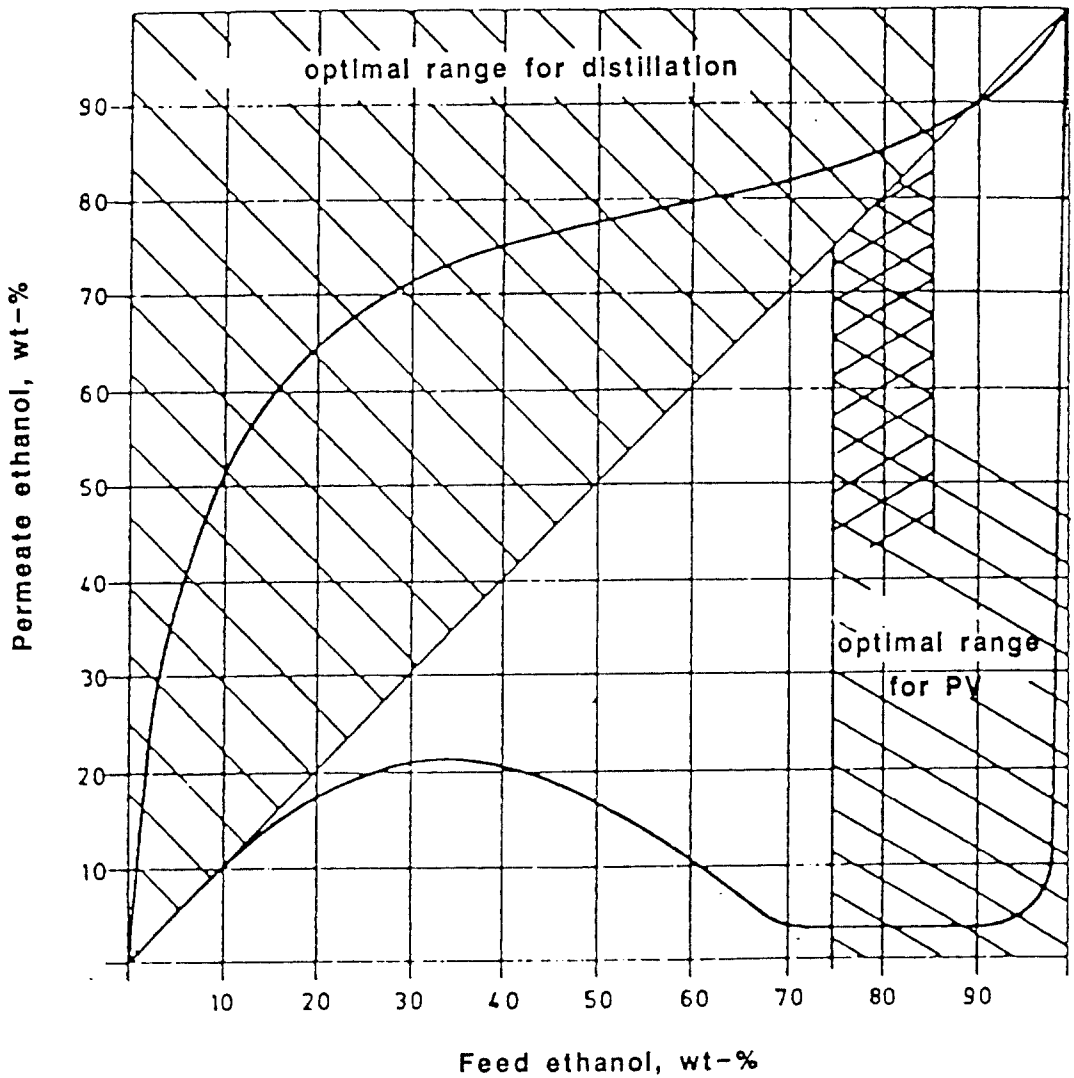


Pervaporation

- > Dehydration of Ethanol**
- > VOC Removal from Water**
- > Hybrid System**

Table XV Density and Osmotic Pressure Data for the System
EtOH-H₂O at 20°C (70)

EtOH wt. %	Density g/cm ³	Osmotic Pressure psi
0	0.9982	0
0.5	0.9973	37
1.0	0.9963	75
1.5	0.9954	111
2.0	0.9945	149
2.5	0.9936	188
3.0	0.9927	230
3.5	0.9918	272
4.0	0.9910	312
4.5	0.9902	356
5.0	0.9893	400
5.5	0.9885	440
6.0	0.9878	486
6.5	0.9870	531
7.0	0.9862	573
7.5	0.9855	621
8.0	0.9847	671
8.5	0.9840	722
9.0	0.9833	774
9.5	0.9826	829
10.0	0.9819	886
11.0	0.9805	996
12.0	0.9792	1103
13.0	0.9778	1218
14.0	0.9765	1330
15.0	0.9752	1460
16.0	0.9739	1600
17.0	0.9726	1748
18.0	0.9713	1905
19.0	0.9700	2061
20.0	0.9687	2235
22.0	0.9660	2612



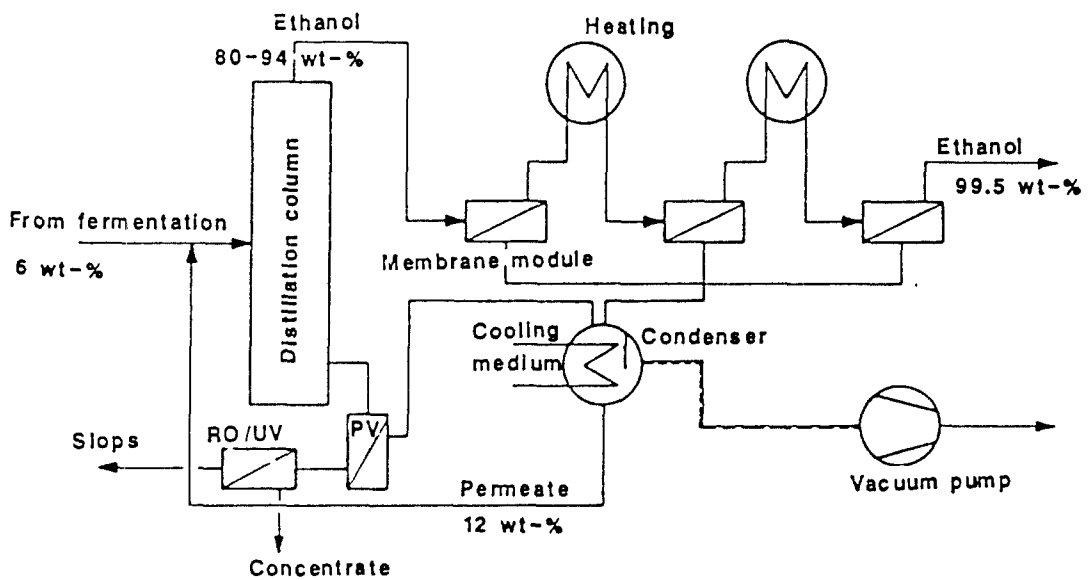


Table 42. GC-MS Analytical Results^[342]

		Feed ^a		Permeate ^a	Boiling point, °C
		Sample 1	Sample 2		
1	Acetic acid, Ethyl Ester	0.2		4.5	77.1
2	1-Propanol, 2-Methyl-			6.8	108.0
3	1-Butanol	14.6	15.0	228.5	117.2
4	Propionic acid, Ethyl Ester	0.25	0.25	11.0	99.1
5	Ethane, 1,1-Diethoxy-			53.3	
6	1-Hexene, 4-Methyl-	1.4	0.7	34.0	87.5
7	Propionic acid	2.3	5.1	2.1	141
8	Propionic acid, 2-Methyl, Ethyl Ester	0.2		15.3	109-111
9	Hexanal	2.3	1.5	33.1	128
10	2-Furfural	2.5	1.4	0.1	161.7
11	Propanoic acid, 2-Methyl-	5.0	7.2	11.2	153.2
12	2-Hexanal	9.8	9.2	224.7	140-147
13	Butanoic acid, 3-Methyl-, Ethyl Ester	0.5	0.5	4.0	
14	1-Hexanol	7.4	6.3	91.2	158
15	1,3-Dioxolane, 2-Ethyl-			5.9	
16	1,3-Dioxolane, 2-Propyl-			0.6	
17	3-Heptanol, 3-Methyl-	0.6	0.5	5.3	163
18	Ethanone, 1-Phenyl-	100.0	100.0	100.0	
19	Hexane, 1,1-Diethoxy-			4.7	
20	Hexane, 1-(1-Ethoxyethoxy)-			1.2	
21	2-Furfural, 5-(Hydroxymethyl)-	28.4	33.2		114-116

^a peak ratio (%) of flavor component
to the internal standard (Ethanone, 1-Phenyl-)

Table 40. Permeate Composition and Permeate Flux Data
of Pervaporation for Benzene Separation^[341]

Operating conditions: temperature, 40°C; downstream pressure, 2000 Pa;
feed flow, 6 L/min; feed volume, 22.7 L;
total benzene content in feed, 30-32 mL

Time, h	Total permeate benzene conc., %	Permeate benzene phase, mL	Permeate aqueous phase, mL	Total weight of permeate sample, g	Permeate flux, kg/m ² h
MTR-100					
1	17.2	26	11135	0.75	
2	4.3	5	102	104	0.58
3	1.0	2	101	102	0.57
4	0.2	*	102	101	0.56
MTR-200					
2	45.4	27	29	53	0.15
4	6.7	1.8	23	24	0.063
6	2.7	0.5	23	23	0.063

*This sample contained only one phase.

Table IX Future Potial in Pervaporation Processes (17)

Applications which are currently possible.

Dehydration of Binary Mixtures

Azeotropic mixtures (isopropyl alcohol/H₂O,
butyl alcohol/H₂O, tetrahydrofuran/H₂O,
ethyl alcohol/H₂O)

Nonazeotropic mixtures (methyl alcohol/H₂O,
acetone/H₂O)

Dehydration of small quantity of water (methylene
chloride/H₂O, chloroform/H₂O)

Dehydration of Mulicomponent Mixtures such as
(ethyl alcohol/toluene/isopropyl alcohol/H₂O,
ethyl esters/methyl esters, H₂O)

Dehydration of Other Solutions

such as (fruit juices, kerosene)

Removal of Organic Solutes from Aqueous Solutions

such as (phenol/H₂O, chlorinated hydrocarbons/H₂O)

Removal of Organic Solvents

from (waste water, fermentation broth)

Dealcoholization of beer and wine

Commercial Applications Possible Within 5 years

Dehydration of Acids and Amines

for example (acetic acid, hydrazine)

Cleaning of Organic Solvents

for example (removal of isopropyl alcohol
from heptane/hexane mixture)

Separation of Paraffins and Aromatic Hydrocarbons

such as (benzene/hexane)

Separation of Chlorinated Hydrocarbons and
Hydrocarbons

Separation of Normal and Branched Hydrocarbons

such as (iso-octane/hexane)

Commercial Applications Are Possible Within 10 Years

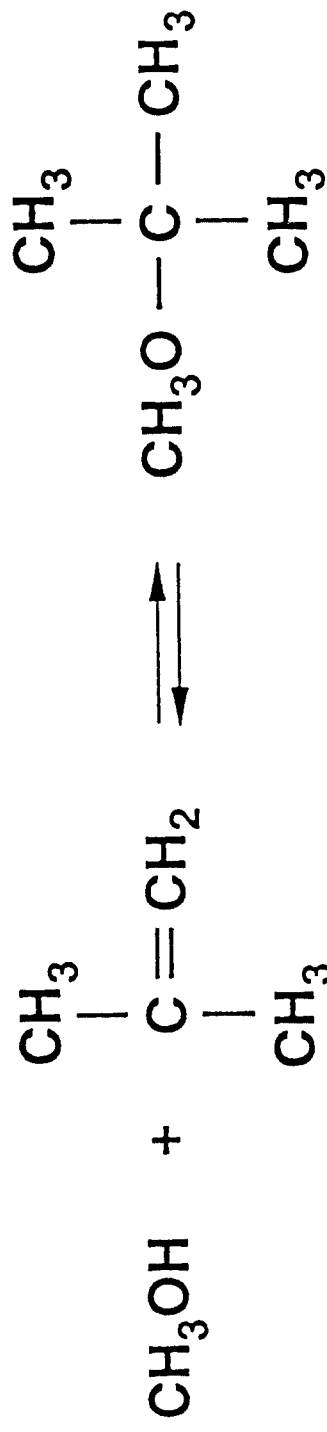
Separation of Paraffins and Olefines

such as (butane/butenes)

Separation of Isomeric Mixtures

such as (xylene mixtures)

Removal of Toxic Substances From Blood Stream



METHANOL

ISOBUTENE

METHYL TERT-BUTYL ETHER

