Membrane contactor and Carbon Dioxide Separation

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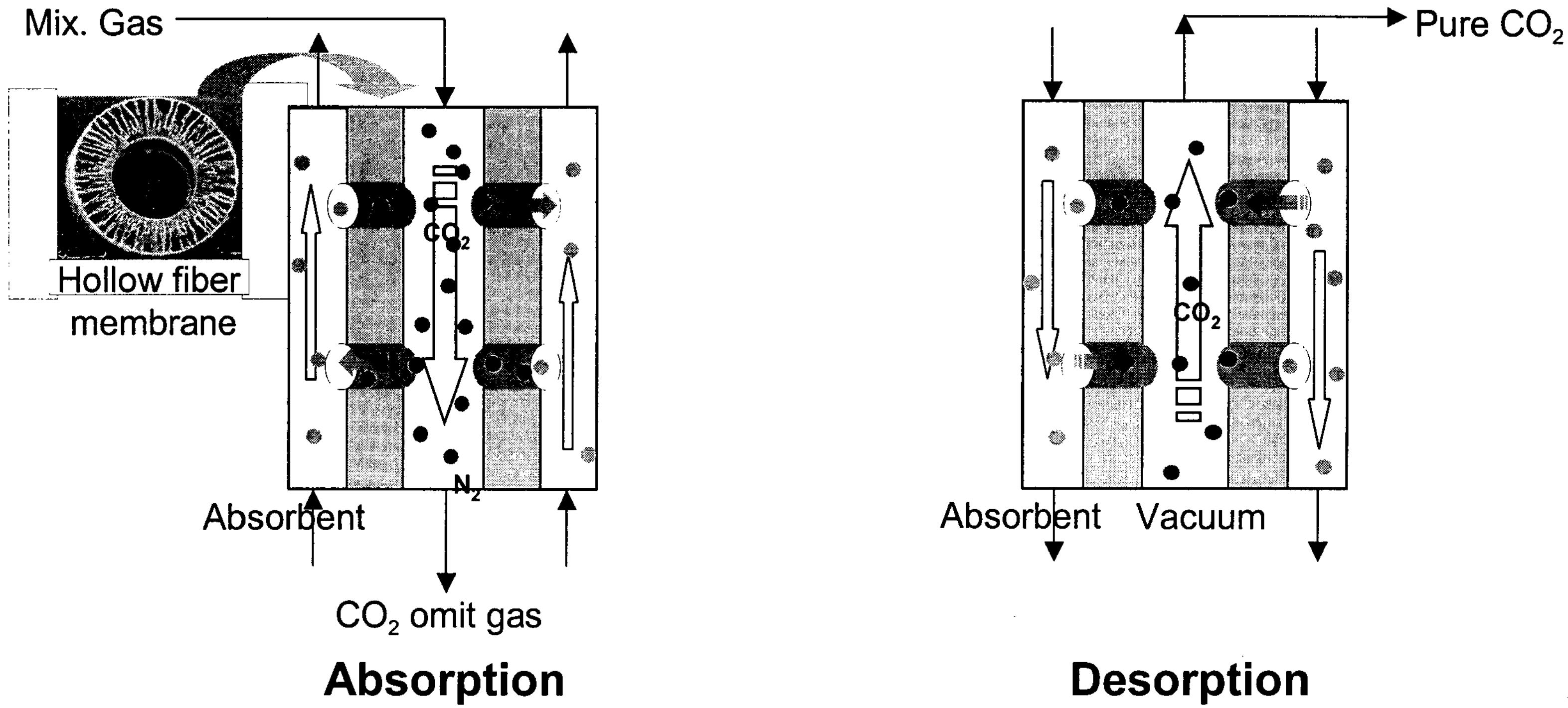
Part 1 Membrane contactor

Membrane contactor

A membrane contactor is a device that achieves gas/liquid or liquid/liquid mass transfer without dispersion of one phase within another.



Membrane contactor processes

- **Membrane Absorption(MA)/Desorption(MD)**
  - Gas absorption and stripping(CO_2, SO_2, H_2S, NH_3 • • •.)
  - Supercritical extraction
  - Waste water treatment

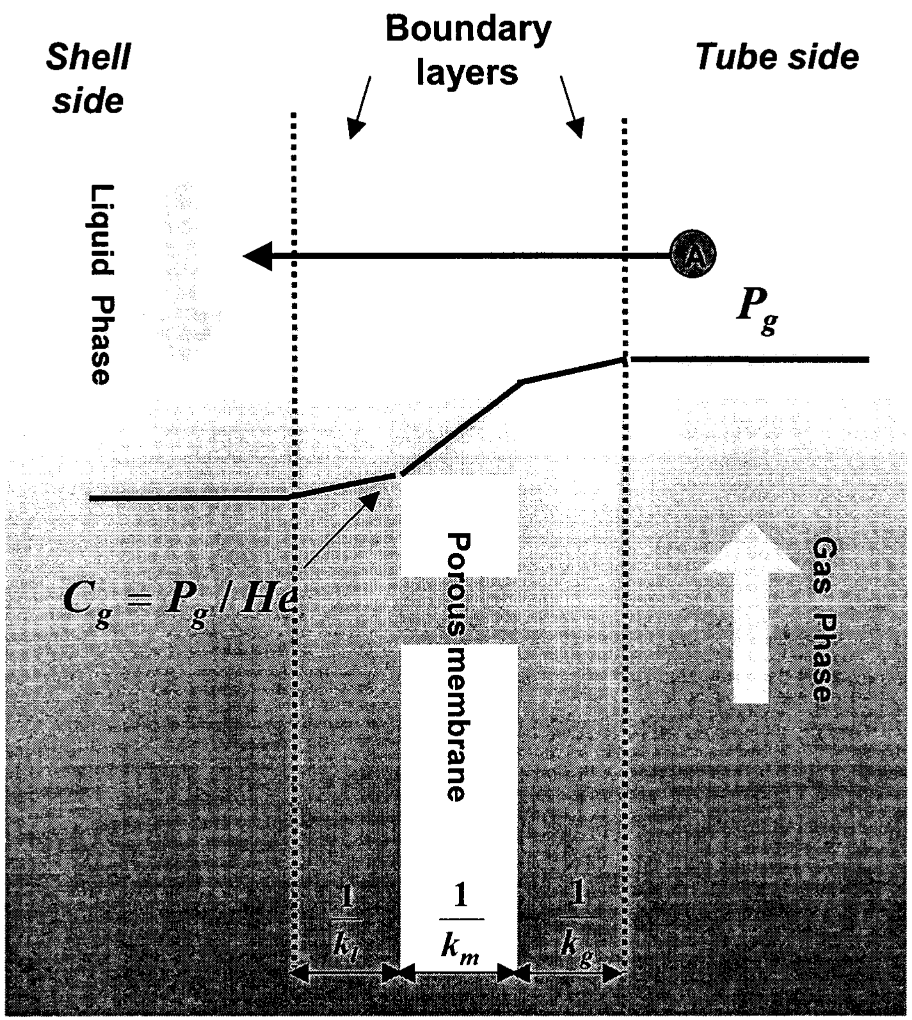
- **Membrane Solvent Extraction(MSX)**
  - Pharmaceutical application
  - Protein extraction
  - Metal ion extraction

- **Membrane Distillation(MD)**
  - High purity water production

- **Liquid Membrane(LM)**
  - Immobilized Liquid Membrane(ILM/SLM)
  - Contained Liquid Membrane(CLM)

- **Membrane Reactor**
  - Chiral separation
  - Fermentation and enzymatic transformation

Film model for membrane contactor



Solute Mass Flux (N_A)

$$N_A = K_L(C_{A,i} - C_{A,L})$$

K_L : Overall mass transfer coefficient
$C_{A,i}$: Concentration of A in interface
$C_{A,L}$: Concentration of A in liquid phase

Overall resistance

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_m} + \frac{1}{k_g}$$

Advantages of membrane contactor

- Separation process not influenced by gas-liquid ratio
- No entrainment, flooding, foaming or channeling
- High specific surface area through use of small size hollow fiber membranes
- Use of modular equipment
- Operation of independent gravity

Comparison of interfacial area per unit volume(ft^2/ft^3) for various types of contactors

contactor	Interfacial area per unit volume(ft^2/ft^3)
Free dispersion columns	1 - 10
Packed/trayed columns	10 - 100
Mechanically agitated columns	50 - 150
Membranes	500 - 2000

(Reed et al., Membrane Separations Technology. Principles and Applications, Elsevier, Amsterdam, 1995, p. 474.)

Paper

-J. of Membrane Science, J. of Applied Polymer Science, Macromolecules, J. of Polymer Science etc.

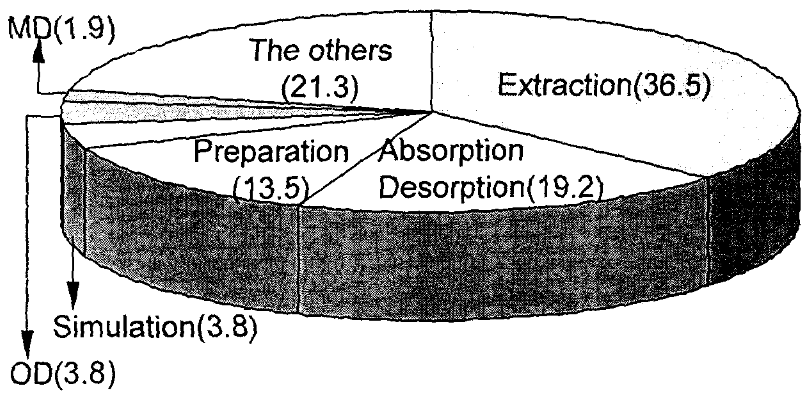


Fig. 연구분야별 분리막 접촉기에 대한 적용 공정 비율(1984-2001)

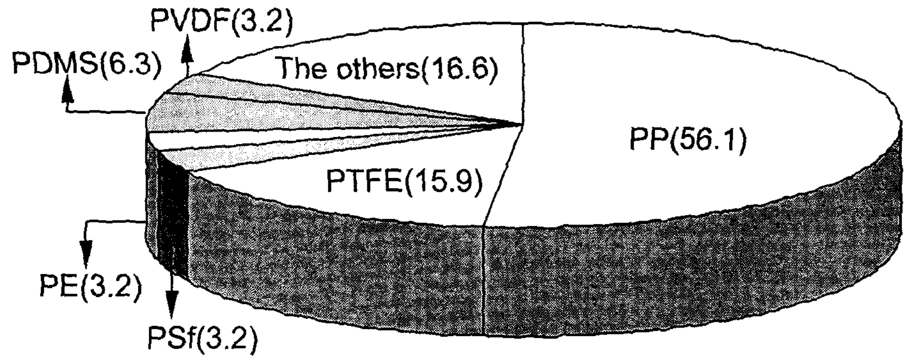


Fig. 연구분야별 분리막 접촉기의 적용 소재 비율(1984-2001)

Patent

- US patent, Japan patent

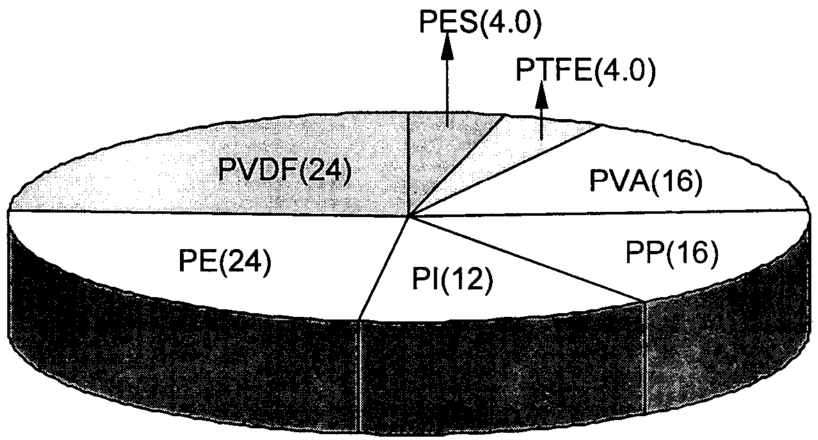


Fig. 연구분야별 분리막 접촉기의 적용 소재 비율(1984-2001)

Material 선정의 요소

-Surface tension(표면장력)

-Thermal stability(열적 안정성)

- Mechanical stability(기계적 안정성)

-Chemical stability(화학적 안정성)

- Pore size(기공 크기)

- Porosity(기공율)

Contac angles of water droplets on polymer materials

- Laplace-Young's equation

$$P = \frac{2\sigma \cos\theta}{\gamma}$$

P : breakthrough pressure
θ : contact angle
σ : surface tension
γ : radius of pore in microporous membrane

Polymer	Contact angle(θ)
PTFE	120
PDMS	105
PP	86
PE	82
PVDF	100
PSf	71
CA	22

* Breakthrough Pressure for PP membrane with pore size of 0.1 μm in contact with water : 150 psig

Methods for preparation of membrane contactor

1. Melt Spinning and Cold Stretching(MSCS) Method

a. Spinning or extrusion of oriented dense membrane

b. Annealing to enhance the crystalline structure

c. Stretching at room temperature : micropore formation

d. Annealing to relax the stress

Methods for preparation of membrane contactor

2. Thermally-induced Phase Separation(TIPS) Method

a. Melt blending of polymer and diluent

b. Spinning or extrusion

c. Controlled cooling during take-up to induce phase separation

d. Removal of diluent : *micropore formation*

e. Drying

Methods for preparation of membrane contactor

3. Phase Inversion Method

a. Blending of polymer solution and additive

b. Spinning

c. Immersion in coagulation bath

d. Removal of solvent and additive : micropore formation

Comparison of methods for preparation of membrane contactor

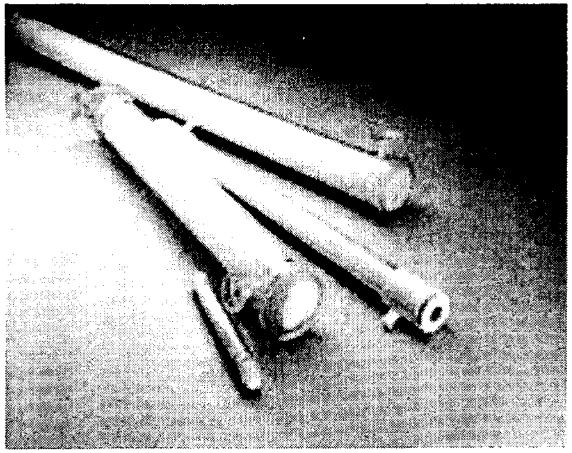
Method	Pore formation	Advantage	Disadvantage
MSCS	Mechanical force by cold-stretching	- Relatively easy handling - No solvent and cleaning process	- Difficult pore size control - Relatively small pore size
TIPS	Removal of diluent	- Relatively easy pore size control	- Waste solvent problem - Relatively complex process
Phase Inversion	Solvent-nonsolvent exchange	- Relatively easy pore size control	- Waste solvent problem

Characteristics of commercially available membrane contactors

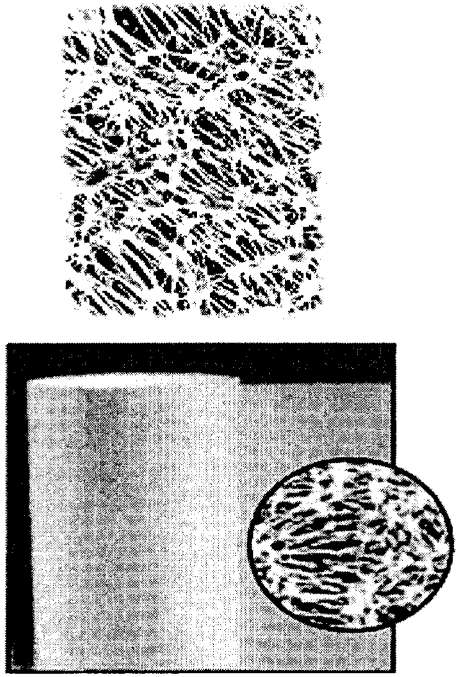
Manufacturer	Material	Fiber diameter (μm)	Pore size (μm)	Porosity
Sumitomo Electric Ind.	PTFE (Polytetrafluoroethylene)	2000	1.0	0.5
Gore-Tex	PTFE (Polytetrafluoroethylene)	1800	2 (max.)	0.5
Desalination System Inc.	PTFE (Polytetrafluoroethylene)	-	0.01-0.5	-
Celgard Inc.	PP(Polypropylene)	300	0.03	0.4
Membrana (Akzo Nobel)	PP(Polypropylene)	400-2000	0.1-0.2	-
Memtec	PP(Polypropylene)	-	-	-
Asahi Kasei	PP (Polypropylene)	-	-	-

Characteristics of commercially available membrane contactors

Manufacturer	Material	Fiber diameter (μm)	Pore size (μm)	Porosity
A/G Technology	PSf(Polysulfone)	0.25-3	1000 MWCO-0.65 μm	-
Koch membrane Systems	PSf (Polysulfone)	0.5-3.2	1000 MWCO-0.2 μm	-
Millipore	PSf (Polysulfone)	0.5-1.1	3000 MWCO-0.1 μm	-
	PVDF(Polyvinylidenefluoride)	-	0.22	0.75
Mitsubishi rayon	PE(Polyethylene)	-	0.1-0.4	-
Dainippon Ink & Chem. Co.	PMP (Polymethylpenten)	215	-	-

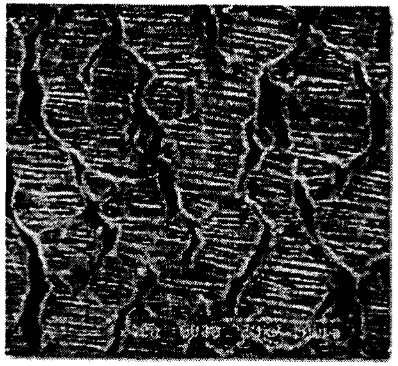


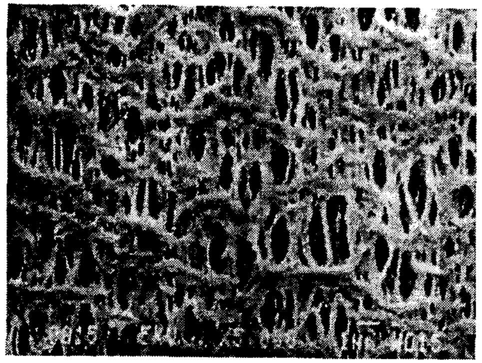
Hollow fiber cartridges(PSf)
(Millipore, US)



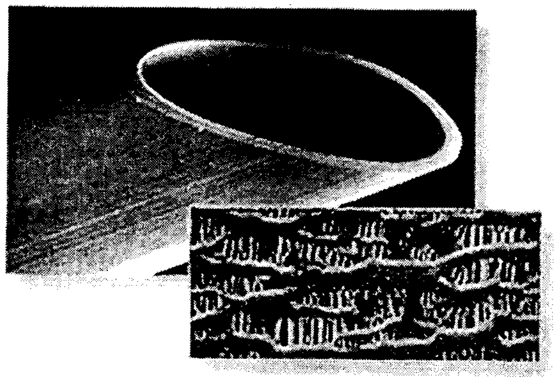
Gore-Tex®
membrane(PTFE)
(Gore-Tex, Japan & US)

Acculel® membrane(PP, PES)
(Membrana, EU)


Poreflon(PTFE)
(Sumitomo Electric Ind., Japan)


STERAPORE™(PE)
(Mitsubishi Rayon, Japan)


SEPAREL®(PMP)
Dainippon Ink & Chemicals, Japan)


Liqui-Cel®(PP)
(Hoechst Celanese Co., US)

The Liqui-Cel(TM) Extra-Flow membrane contactor from CELGARD LLC. The central baffle minimizes shell side bypassing and provides a component of velocity normal to the fibers

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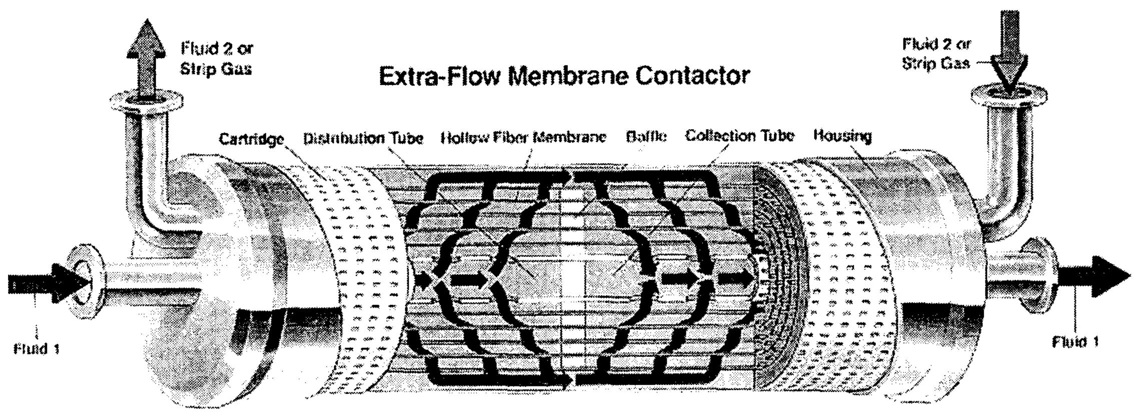


Part 2. Carbon Dioxide Separation using Membrane contactor (KRICT)

Introduction

Symmetric Hollow Fiber Membrane

- Poly(tetrafluoroethylene)(PTFE), Polypropylene(PP)
  - TIPS (Thermally-Induced Phase Separation)
  - MSCS (Melt Spinning and Cold Streching)

Symmetric Structure

▼

High Membrane Resistance

Asymmetric Hollow Fiber Membrane

- Poly(vinylidene difluoride(PVDF), polysulfone(PSf)
  - Phase Inversion Process

Asymmetric Structure

▼

low Membrane Resistance

Mass transfer coefficient (W.K. Teo)

- Porous Asymmetric Hollow Fiber Membrane(PS_f)

﹀ *2-8 times higher*

- Porous Symmetric Hollow Fiber Membrane(PP)

Objectives

Preparation of asymmetric PVDF hollow fiber membranes with high permeability and good hydrophobicity for membrane contactors

PVDF,Poly(vinylidene fluoride) Hollow Fiber Membrane

• Asymmetric Structure
: *Loeb-Sourirajan* Phase Inversion Method

- High Flux
- Easily pore size control
- Good Hydrophobicity
- Good Chemical Resistance
- Good Oxidant Resistance

Experimental

Materials

- Polymer : Polyvinylidene fluoride(PVDF, Kynar grade 761)
- Solvent : Dimethlacetamide(DMAc, Merck, > 99%)
- Additives : Lithium Chloride(LiCl), Zinc Chloride($ZnCl_2$)
- Coagulants : Water(internal, external), DMAc/Water mix.(internal)
  EtOH/Water mix.(internal)
- Absorbents : Pure Water, 5wt% MEA

Test Cell & Module

- Test Cell : Stainless Steel (Inner diameter : 45mm)
- Test Module : Sus Tube (12 X 300mm)
- Hollow Fiber Membrane Contactor : Acryl Tube
  : Volume : 7.22 X 10^{-5} m(20 X 250mm)

Packed Column

- Packing Materials : 1/2" Rasching ring
- Column Volume : 11.45 X 10^{-5} m

Dimensions of membrane contactors and Packed column

		Packed Column	PTFE Module	PVDF Module	PP Module
Diameter		0.027	0.02 m	0.02 m	0.02 m
Length		0.2	0.23 m	0.23 m	0.23 m
Surface Area		710 m^2/m^3	1339.5 m^2/m^3	1488.1 m^2/m^3	2855.29 m^2/m^3
Contact Area		710 m^2/m^3	937.64 m^2/m^3	?	1998.7 m^2/m^3
Volume		114.45 cm^3	72.2 cm^3	72.2 cm^3	72.2 cm^3
Fiber	**I.D.**		1000 μm	830 μm	250 μm
	O.D.		1913 μm	1070 μm	550 μm
	Pore size		1 μm	0.03 μm	0.25 μm
	Porosity		70 %	?	70 %
	Packing density		0.64	0.4	0.4
	Number of fiber		70	139	519

Results & Discussion

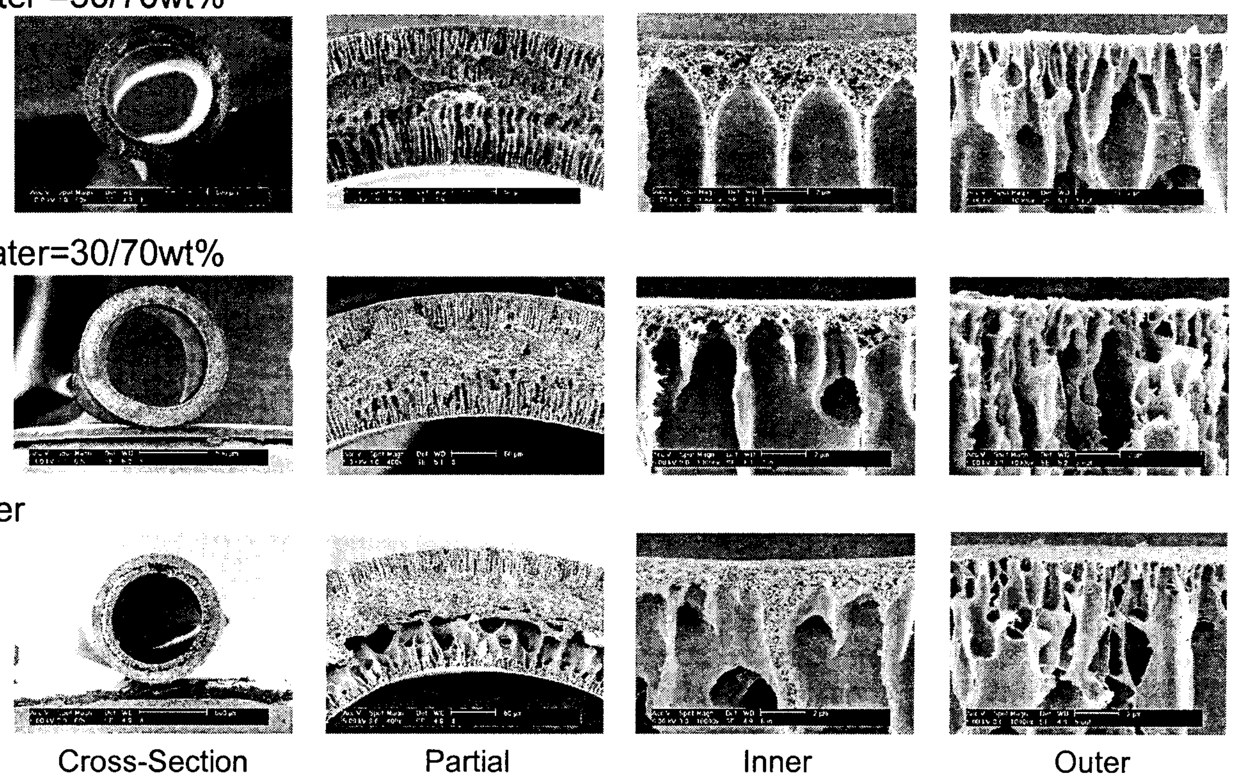
Effect of Internal Coagulant(PVDF Hollow Fiber Membrane, KRICT)

* PVDF/LiCl/DMAc=13/7/80wt%
* Outer Coagulant : pure water

1) EtOH/Water =30/70wt%

2) DMAc/Water=30/70wt%

3) Pure Water



Permeation properties and pore structure parameters of PVDF and commercialized PP, PTFE hollow fiber membranes

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* PVDF : KRICT (PVDF/LiCl/DMAc=13/7/80wt%)
* PP : M- Memtec, C- Celgard
* PTFE : *Sumitomo*

Membrane	OD,ID(μm)	P_{N2}	r(m)	$\varepsilon/L_p(m^{-1})$
PVDF-①	1106,801	$1.3X10^{-3}$	$1.5X10^{-8}$	$1.84X10^{4}$
PVDF-②	1073,830	$7.5X10^{-4}$	$3.0X10^{-8}$	$2.95X10^{3}$
PVDF-③	933,670	$6.5X10^{-4}$	$3.1X10^{-8}$	$2.82X10^{3}$
PP-M	550,250	$2.1X10^{-4}$	$3.0X10^{-7}$	$5.14X10^{2}$
PP-C	329,270	$1.1X10^{-4}$	$1.9X10^{-8}$	$1.16X10^{3}$
PTFE	1913,1000	4.8	$1X10^{-6}$	

* Internal Coagulants :

PVDF-① : EtOH/water=30/70%, ② : DMAc/water=30/70%, ③ : Pure water

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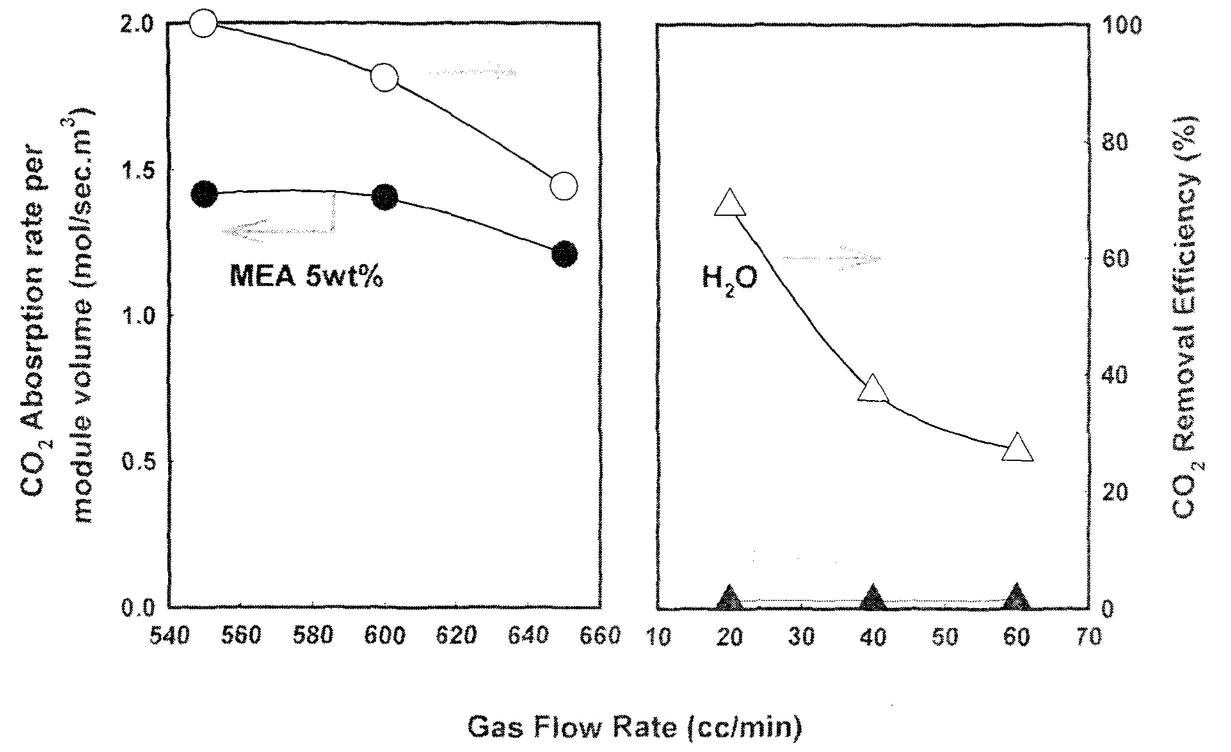
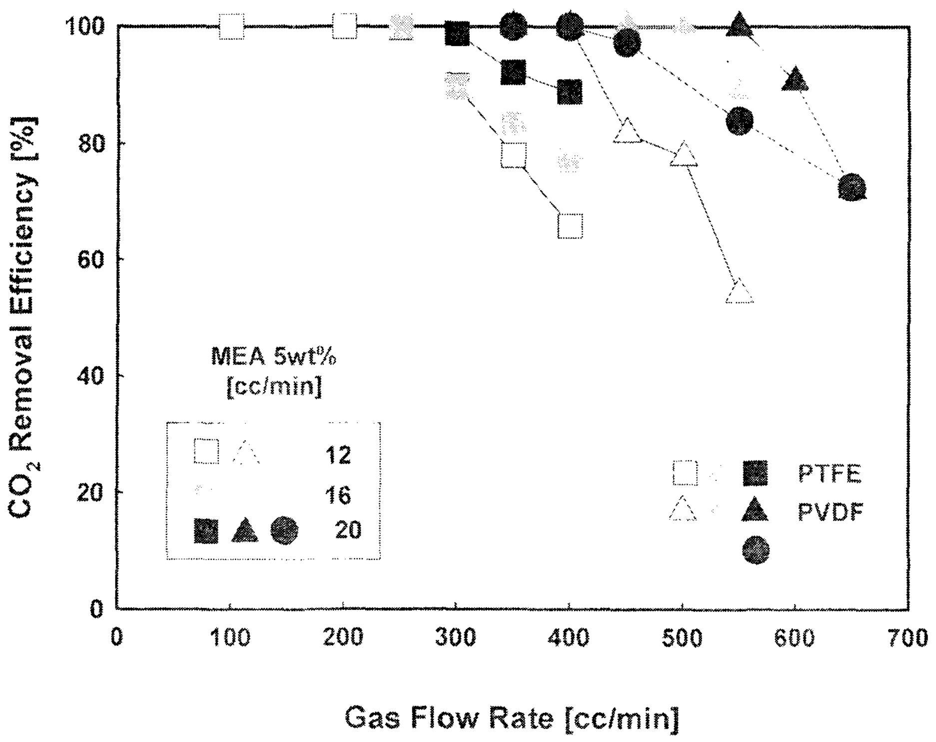
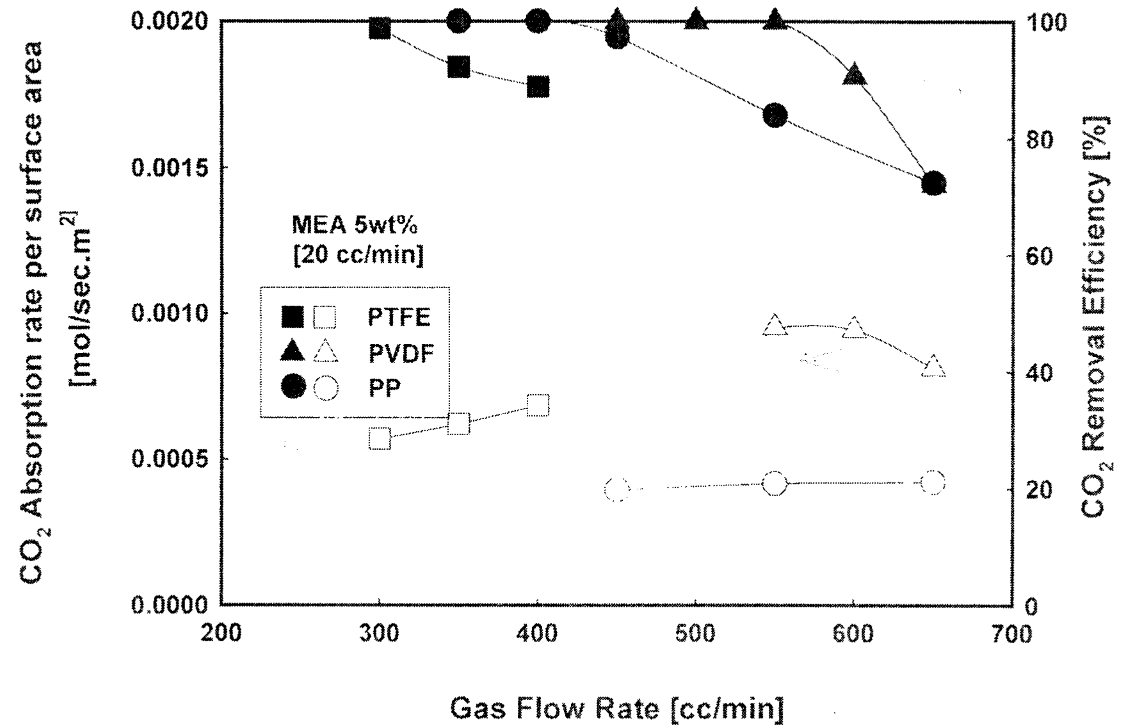
Comparison of CO_2 absorption rate per module volume of PVDF hollow fiber membrane contactors and removal efficiency in MEA 5wt% and H_2O as absorbent for various gas flow rate



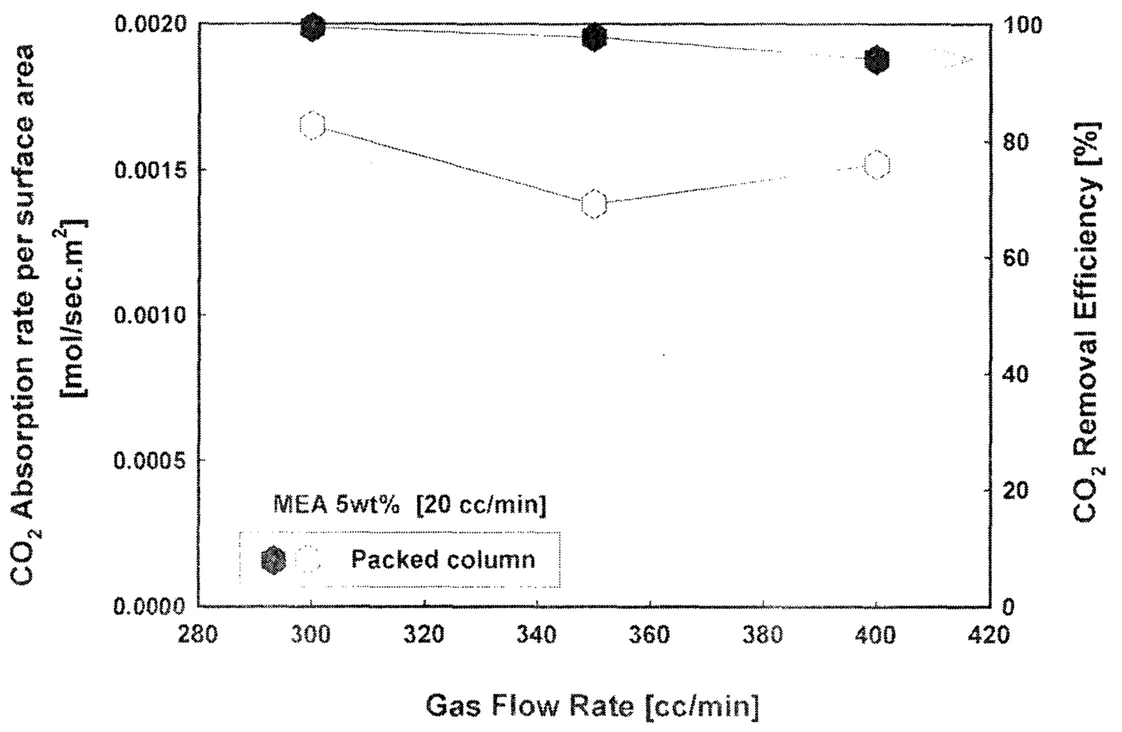
Comparison of CO_2 removal efficiency rate in PTFE, PVDF and PP hollow fiber membrane contactors for various absorbent(MEA 5wt%) flow rate



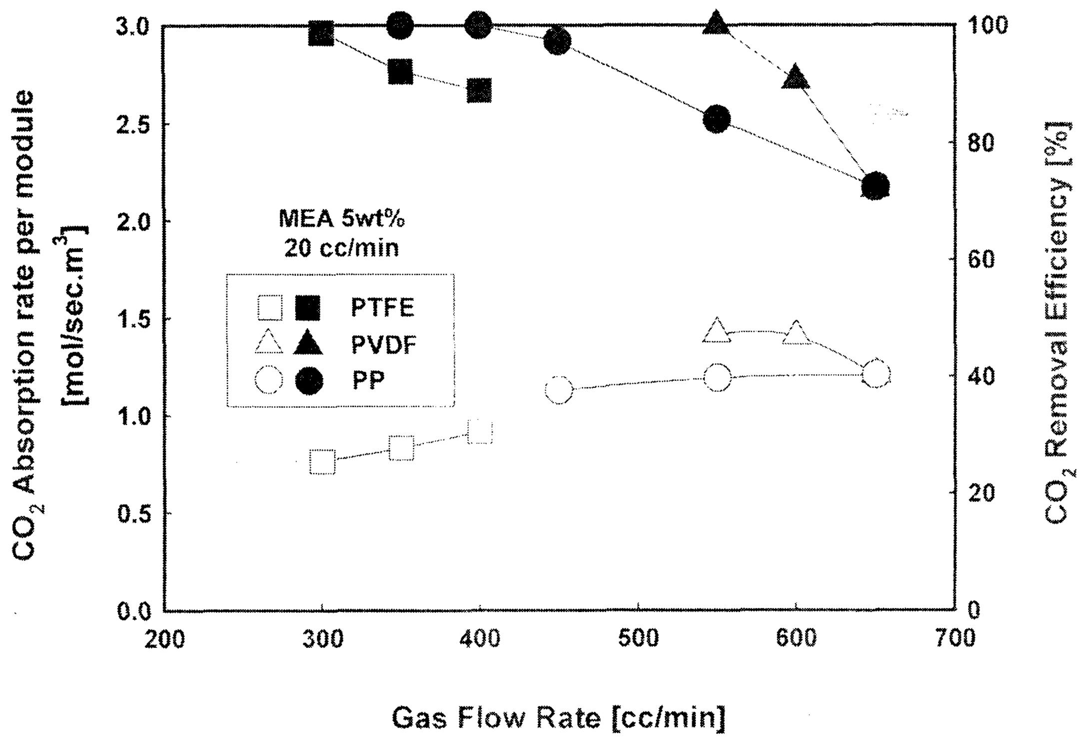
Comparison of CO_2 absorption rate per surface area of membrane and removal efficiency in PTFE, PVDF and PP hollow fiber membrane contactors for various absorbent(MEA 5wt%) flow rate



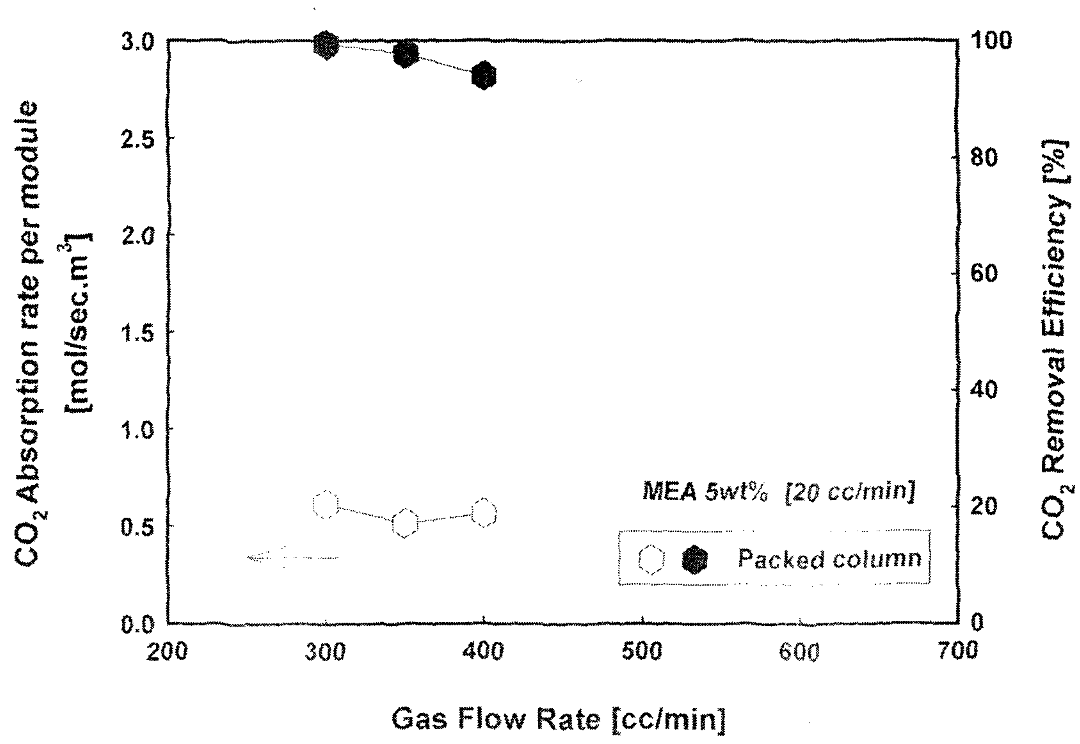
CO_2 absorption rate per surface area of membrane and removal efficiency in Packed column for various absorbent(MEA 5wt%) flow rate



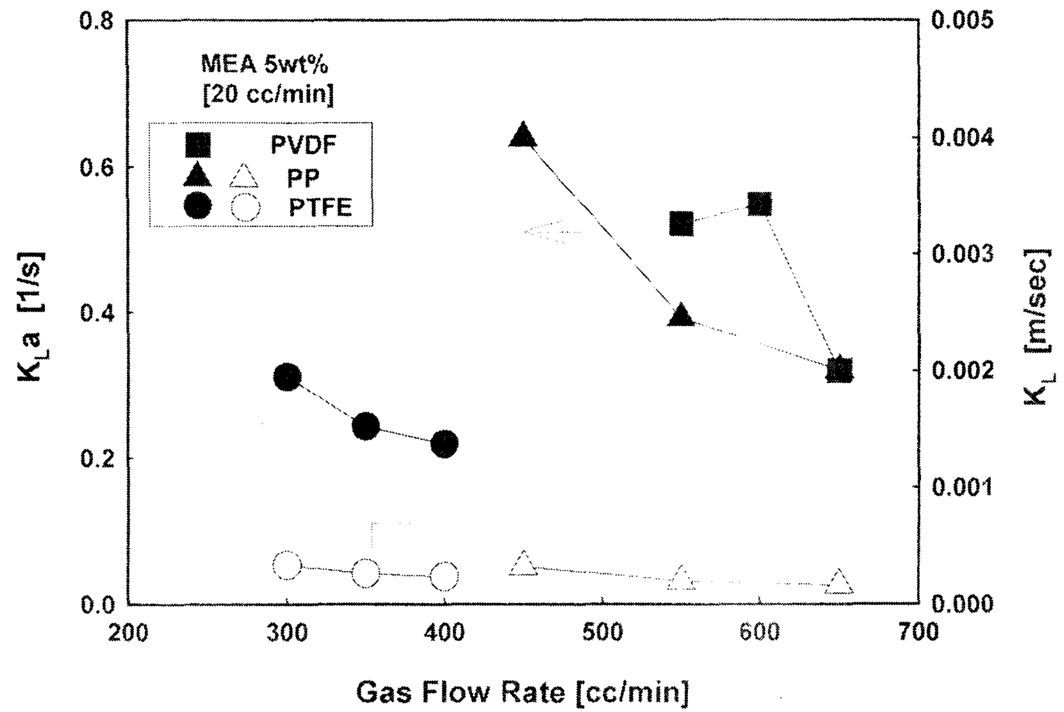
Comparison of CO_2 absorption rate per module volume and removal efficiency in PTFE, PVDF and PP hollow fiber membrane contactors for various absorbent(MEA 5wt%) flow rate



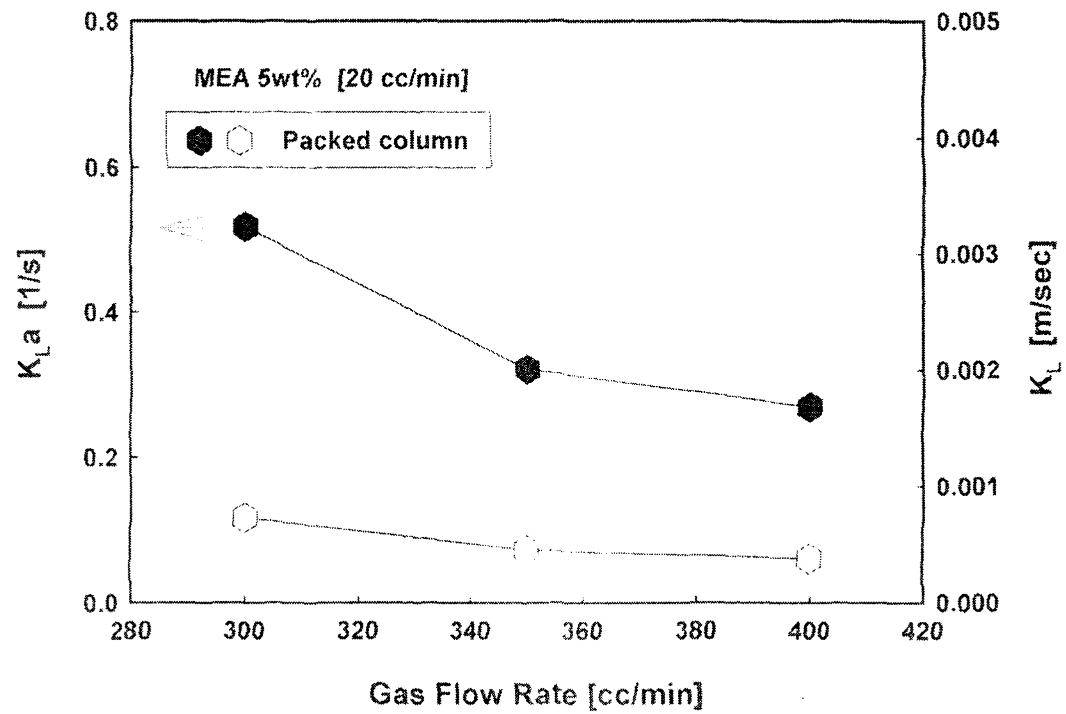
CO_2 absorption rate per module volume and removal efficiency in Packed column for various absorbent(MEA 5wt%) flow rate



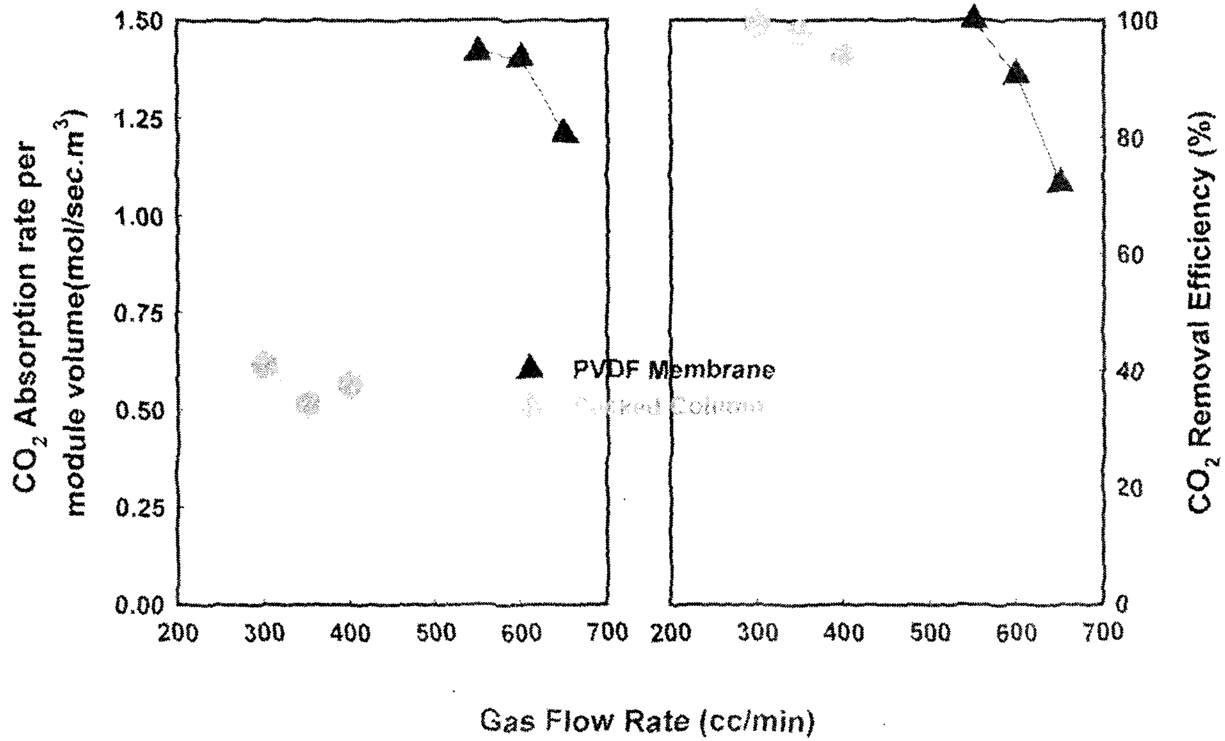
Comparison of overall mass transfer coefficient(K_La, K_L) in PTFE, PVDF and PP hollow fiber membrane contactors for various absorbent (MEA 5wt%) flow rate



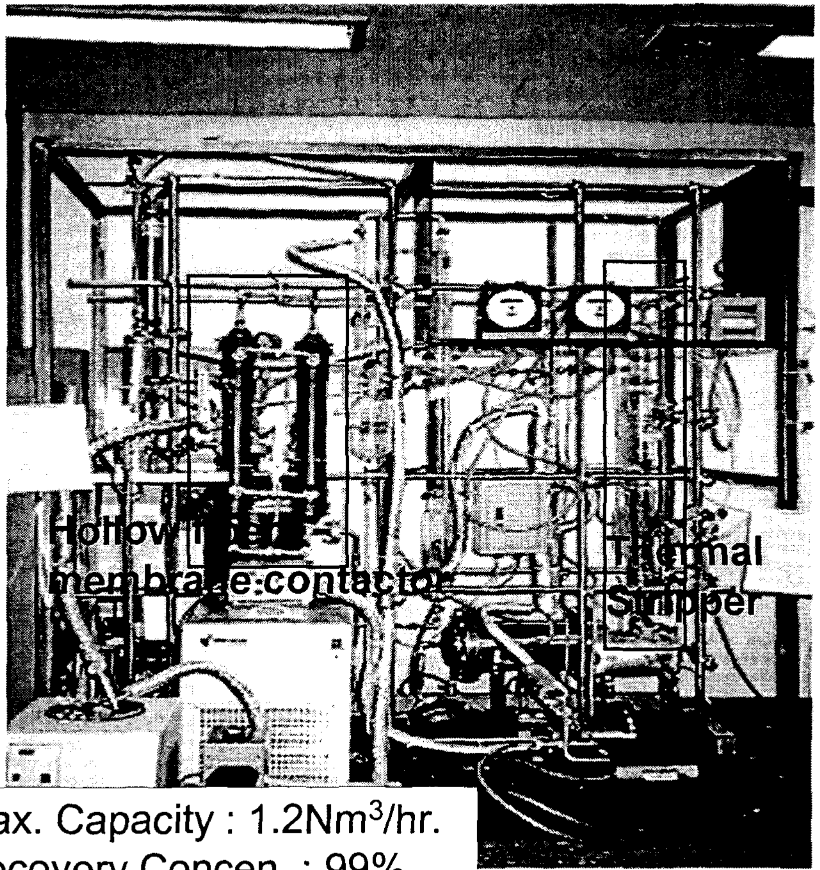
Overall mass transfer coefficiency(($K_L a$, K_L) in Packed column for Various absorbent(MEA 5wt%) flow rate



Comparison of CO_2 absorption rate per module volume and removal efficiency in PVDF hollow fiber membrane contactor and Packed column for various gas flow rate

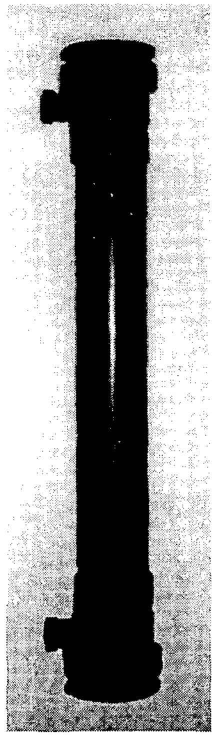


Hybrid system(KRICT)



Max. Capacity : 1.2Nm^3/hr.
Recovery Concen. : 99%

Hollow Fiber Membrane
Contactor Module



- I.D : 4 inch
- Length : 60 cm

Summary

- PVDF is good material for a hollow fiber membrane with high porosity and excellent hydrophobicity.
- Asymmetric PVDF hollow fiber membranes were prepared by the Loeb-Sourirajan phase inversion method.
- Asymmetric PVDF hollow fiber membranes could be controlled in pore size and porosity using various additives(LiCl, $ZnCl_2$) and internal coagulants (water, EtOH/water, and DMAc/water mixture).
- CO_2 removal efficiency of asymmetric PVDF hollow fiber membranes was 1.2 times higher than that of commercialized PP hollow fiber membranes at MEA 5wt% solution.
- CO_2 flux of asymmetric PVDF hollow fiber membranes was 2.5 times higher than that of commercialized PP hollow fiber membranes.
- CO_2 removal efficiency and absorption rate of asymmetric PVDF hollow fiber membranes were 30 times higher than those of packed column at absorbent H_2O.
- CO_2 flux of asymmetric PVDF hollow fiber membranes at MEA 5wt% solution was 48 times higher than that of pure water.
- In the case of MEA 5wt% solution used as an absorbent, the CO_2 absorption rate and removal efficiency of PVDF hollow fiber membrane were 2.3 times higher than that of a packed column.

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