Pressure Swing Absorption Device and Process for Separating CO_2 from Shifted Syngas and its Capture for Subsequent Storage

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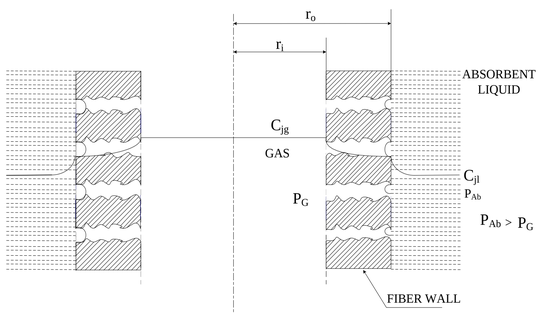
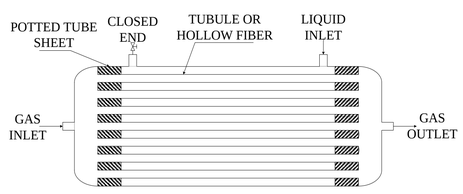
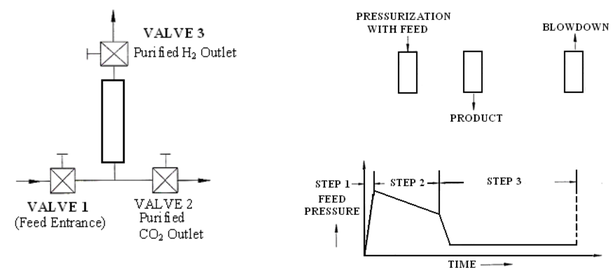
Concentration profile for absorbed species in gas and liquid phases in a membrane contactor



Schematic of the absorber containing ceramic tubules or hollow fibers



Pressure Swing Absorption Operation



Solenoid Valve Locations in Pressure Swing Absorption (PSAB) Apparatus

Pressure vs. time profile in the bore of tubule or hollow fiber in PSAB

(Bhaumik et al., *AIChE J.*, 42, 409-421 (1996))

Potential Advantages of the Proposed Separation Technique-1

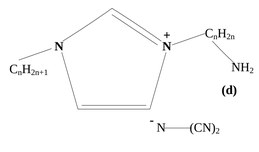
- Has high solubility selectivity of novel selected liquid absorbents having relatively high viscosity
- Has high purification ability of pressure swing adsorption process
- Has high gas-liquid contacting surface area per unit device volume
- Has a compact membrane-like device
- Scale up should be easier due to modularity of membrane-based devices and membrane-based phase contacting

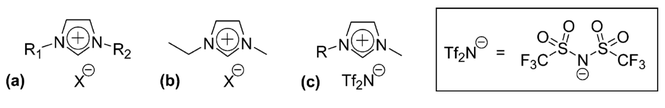
Potential Advantages of the Proposed Separation Technique-2

- Will deliver highly purified H_2 at nearly its partial pressure and temperature in the post-shifted reactor synthesis gas feed
- Purified CO_2 stream (>90% CO_2) will be available at 1-3 atm

Nonvolatile Absorbents for PSAB

1. Ionic Liquids:
[bmim]$^+$[PF_6]$^-$ (Fluka)
[bmim]$^+$[DCA]$^-$ (Merck)
[Am-Im]$^+$[DCA]$^-$ (Functionalized)
(with or without moisture)





General structures of (a) imidazolium-based RTILs, (b) [C_2mim][X] RTILs, and
(c) [Rmim][Tf_2N] RTILs. (Bara et al., *Ind. Eng. Chem. Res.*, 48, 2739 (2009))

Nonvolatile Absorbents for PSAB

2.(a) Dendrimers/hyperbranched polymers of lower molecular weight:
Polyamidoamine (PAMAM) generation 0, MW-516, 4 primary amines, 2 tertiary amines;

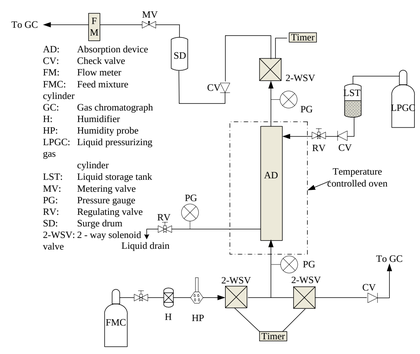
Generation 2, MW-3130
(Dendritech, Midland, MI)
Use in a nonvolatilesolvent,
such as polyethylene glycol (PEG 400)
Highly reactive in the presence of moisture
(1. Kovvali et al., *JACS*, 122 (31) 7594 (2000); 2. Kovvali and Sirkar, *I&E C Res.*, 40(11), 2502 (2001); 3. Kosaraju et al., *I&E C Res.*, 49, 1250 (2005))

(b) Polyethyleneimines of lower molecular weight, Lupasol FG (BASF), MW-615
(Rolker et al., *I&E C Res.*, 46, 6572 (2007)

Adaptation of PSAB Device to the Current Problem

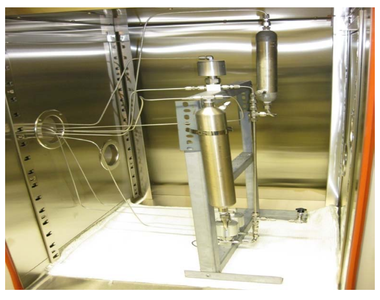
1. Porous PP membrane substrate replaced by hydrophobized porous ceramic tubules, porous PTFE hollow fibers and hydrophobized PEEK hollow fibers (higher temperature, wettability considerations)
2. High pressure means smaller membrane pore size (5 nm to 10 nm) at the gas-liquid interface to prevent any phase breakthrough
3. Longer length of hollow fibers in RAPSAB replaced by number of modules of hollow fiber/ceramic tubules in series (limitation of oven dimensions)

Schematic of the experimental setup for pressure swing absorption



Ceramic Membrane Tubules in Modules and Teflon Modules

Experimental Setup inside the Oven for PSAB



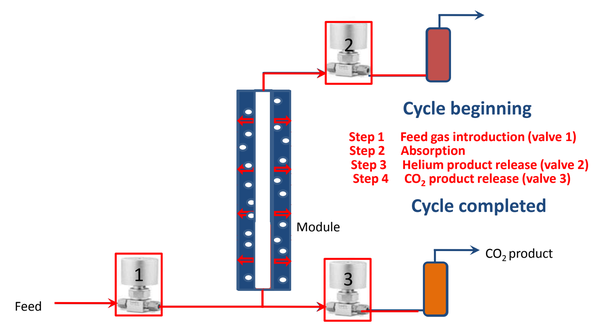
Larger Module containing PEEK Hollow Fibers in the Setup

Liquid Breakthrough Pressure Test Results for Membrane Modules Recently Obtained (Phase II)

	Water	[Bmim][DCA]	[Emim][Tf2N]	PEG 400	20% Dendrimer + DCA
Ceramic #7	210 psi	No leakage up to 300 psi	N/A	300 psi	220 psi
Ceramic #8	No leakage up to 300 psi	No leakage up to 300 psi	180 psi	No leakage up to 300 psi	N/A
PEEK #20 Epoxy	No leakage up to 200 psi	40 psi	N/A	140 psi	N/A
PEEK #21 Epoxy	No leakage up to 200 psi	No leakage up to 140 psi	N/A	180 psi	N/A
2" PEEK (2PG295)	No leakage up to 200 psi	No leakage up to 200 psi	No leakage up to 200 psi	No leakage up to 200 psi	N/A
Teflon* (S/N: 1004)	No leakage up to 100 psi	100 psi	N/A	80 psi	100 psi
Teflon* (S/N: 1005)	140 psi	40 psi	N/A	80 psi	40 psi
Teflon* (S/N: 1006)	No leakage up to 140 psi	60 psi	N/A	80 psi	60 psi

Room temperature, dry air sweep, liquid pressurized with nitrogen; *Epoxy-- O-ring seal

Process of pressure swing absorption for separating CO_2 from shifted syngas: 3-Valve system



PSAB performance comparison between 3-valve and N-valve systems using a PEEK membrane module

Feed gas pressure, psi	Liquid pressure, psi	System	Cycle time/s & Pressure drop/psi		CO_2 content of Helium product	CO_2 content of CO_2 product
100	120	N-valve	97.0; 95.0		8.31%	70.10%
100	120	3-valve	5; 30; 1; 30	97.0; 95.0; 75.0; -28.0inHg	8.00%	38.40%
100	120	3-valve	5; 30; 30; 30	97.0; 95.0; 0; -28.0inHg	30.90%	76.95%
120	130	N-valve	117.0; 115.0		7.16%	67.20%
120	130	3-valve	5; 30; 1; 30	117.0; 115.0; 95.0; -28.0inHg	8.18%	39.60%
120	130	3-valve	5; 30; 30; 30	117.0; 115.0; 0; -28.0inHg	33.00%	76.10%

Feed gas composition: 40.67±2 % CO_2, Helium balance. Liquid used for CO_2 absorption: pure [Bmim][DCA]. All tests were carried out at room temperature about 22°C, and dry feed gas was introduced to the tube side of module. Only one PEEK membrane module (No.1 with product number 30-105-21) was used.

High Pressure High Temperature PSAB Test Results of Ceramic Membrane Module with a Single Tubule (N-Valve System)

Feed gas pressure psi	Liquid pressure psi	Cycle time/s & Pressure drop/psi	CO_2 content of Helium product	CO_2 content of CO_2 product
250 (25°C)	260	5; 30; 240; 235;	32.9~33.0%	43.1~44.2%
250 (25°C)	260	5; 30; 240; 235;	31.6~32.0%	43.1~44.2%
250 (25°C)	260	5; 30; 240; 235;	32.2~32.5%	43.1~44.2%
260 (100°C)	280	5; 30; 255; 252;	33.5~34.0%	44.9~45.5%
260 (100°C)	280	5; 30; 255; 252;	33.5~33.6%	44.9~45.5%
260 (120°C)	280	5; 30; 255; 252;	33.7~33.8%	44.7~44.9%

Feed gas composition: 40.67±2 % CO_2, Helium balance. Liquid used for CO_2 absorption: pure [Bmim][DCA]. For all tests dry feed gas was introduced to the tube side of module.

One ceramic membrane module (#8) was used. (One 1/8 inch Teflon rod was inserted into the ceramic tube to reduce the dead volume).

High Pressure PSAB Runs with Longer PEEK Membrane Module (N-Valve System) (~25°C and 100°C)

Feed gas pressure, psi	Liquid pressure, psi	Cycle time/s & Pressure drop/psi	CO_2 content of Helium product	CO_2 content of CO_2 product
100 (25°C)	120	2; 30; 35; 34;	14.1%	45.7~52.6%
150 (25°C)	160	10; 30; 145; 140;	14.6~15.0%	83.0%
200 (25°C)	220	10; 30; 200; 195;	14.8~15.5%	85.3%
250 (25°C)	270	10; 30 250; 244;	16.7%	63.6~69.6%
250 (25°C)	270	10; 60; 250; 243;	15.0%	63.6~69.6%
100 (100°C)	120	5; 30; 100; 97;	22.9%	56.8~65.2%
150 (100°C)	160	5; 30; 149; 145;	25.3~25.6%	51.4~61.0%
150 (100°C)	160	5; 30; 149; 145;	28.8%	51.4~61.0%

Feed gas composition: 40.67±2 % CO_2, Helium balance. Liquid used for CO_2 absorption: pure [Bmim][DCA]. For all tests dry feed gas was introduced to the tube side of module.

One new longer PEEK membrane module was used.

Solubility Measurement Setup

NJIT New Jersey's Science & Technology University