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

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DOE-NETL Award No. DE-FE0001323
Kick-off Meetings: Pre-combustion CO_2 Control
Pittsburgh, November 13, 2009

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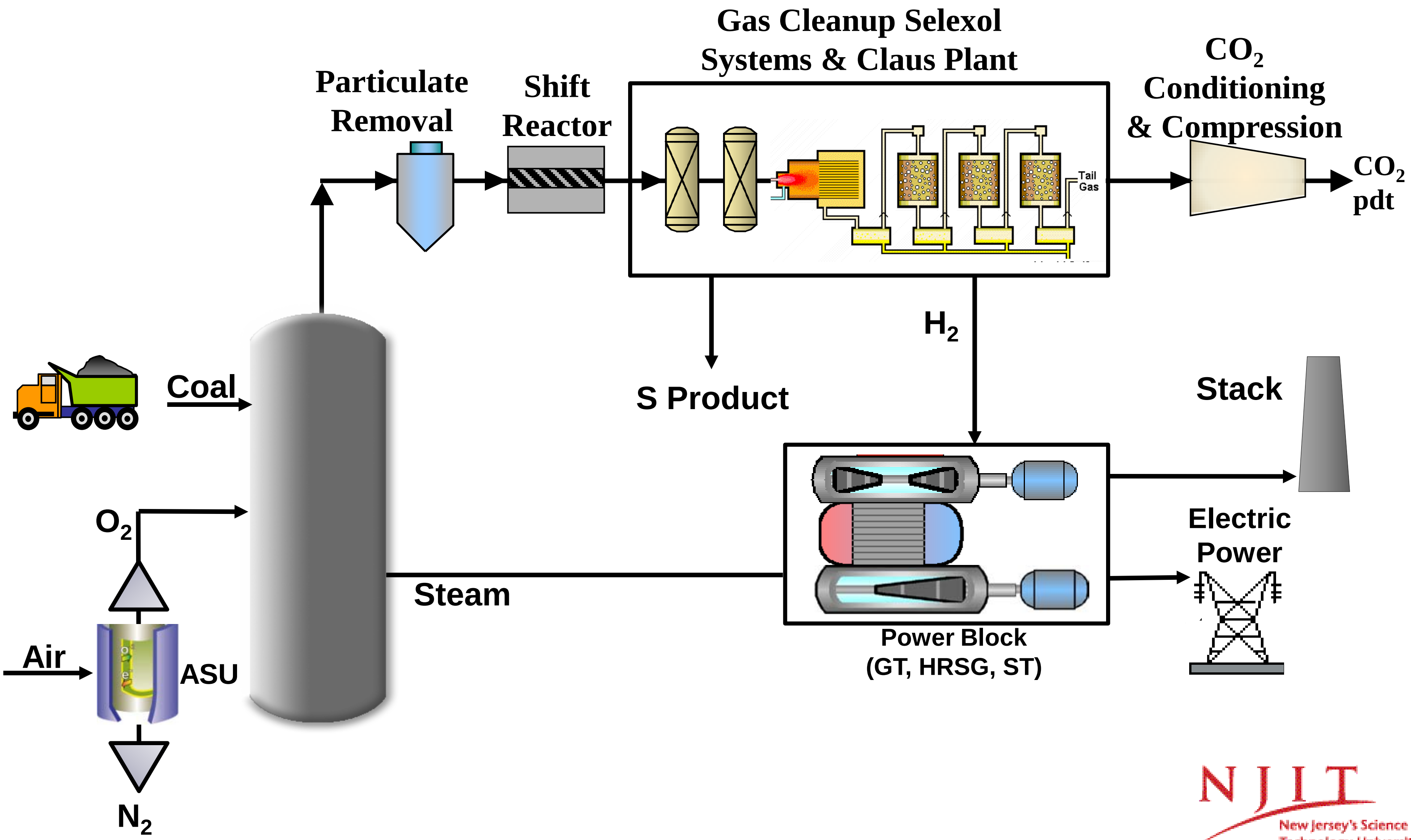
Typical IGCC Plant with a Shift/Selexol based CO_2 Capture System



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- **Background**
- Technology Description

(a) Process and Device Concept

(b) Detailed Considerations on Process and Device

- Project Objective
- Project Structure
- Project Budget
- Project Management Plan including Risk Management

Precombustion CO_2 Capture from Shifted Syngas

1. Typical IGCC plant will employ Selexol-based CO_2 capture:
    - Shifted syngas is cooled, humidified and expanded to recover some energy
    - Double-stage Selexol unit will remove H_2S and CO_2
    - H_2S recovered as elemental sulfur in a Claus unit
    - CO_2 flashed off the absorbent liquid at a lower pressure (~50 psia)

2. Variety of Sorbent-based Process, Ca-based, Hydrotalcite-based etc., Thermal swing sorption-enhanced reaction (TSSER), PSA

3. Membrane Processes:

- Highly H_2-selective metallic or ceramic or zeolitic membranes
- CO_2-selective polymeric membranes
- Membrane reactor for shift gas reaction with CO_2-selective membrane
- Ionic liquid-based supported liquid membranes

4. Pressure swing absorption of CO_2 for post low-temperature shift reactor gas using membrane contactors containing ionic liquids, dendrimers etc.
5. Other processes…

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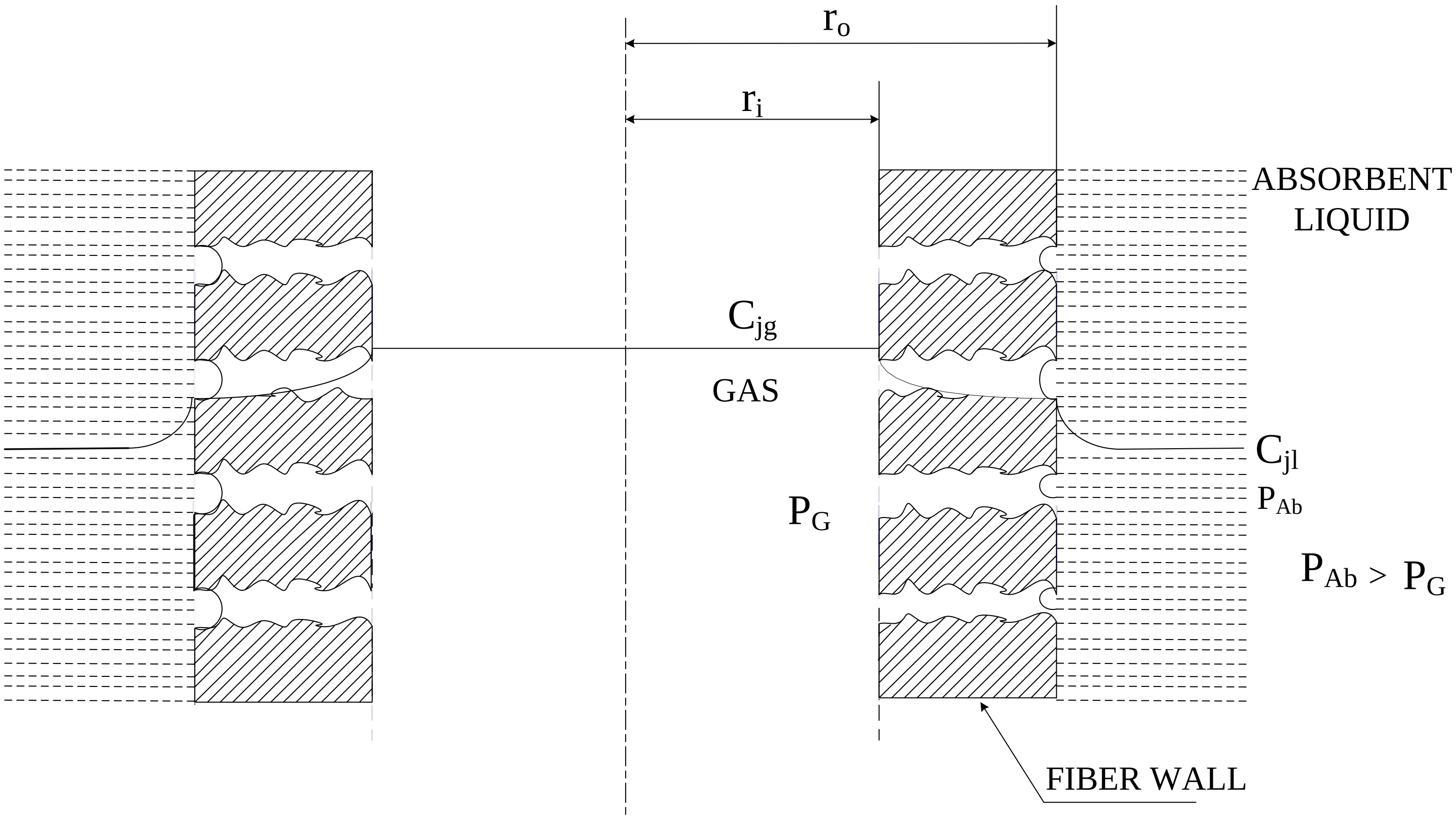
Concentration profile for absorbed species in gas and liquid phases in a membrane contactor



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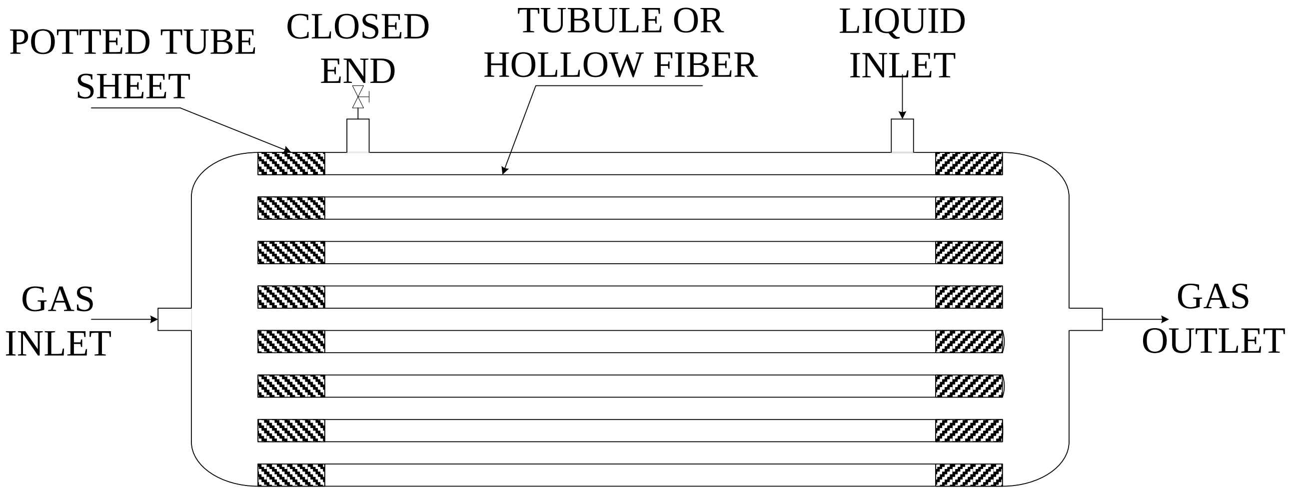
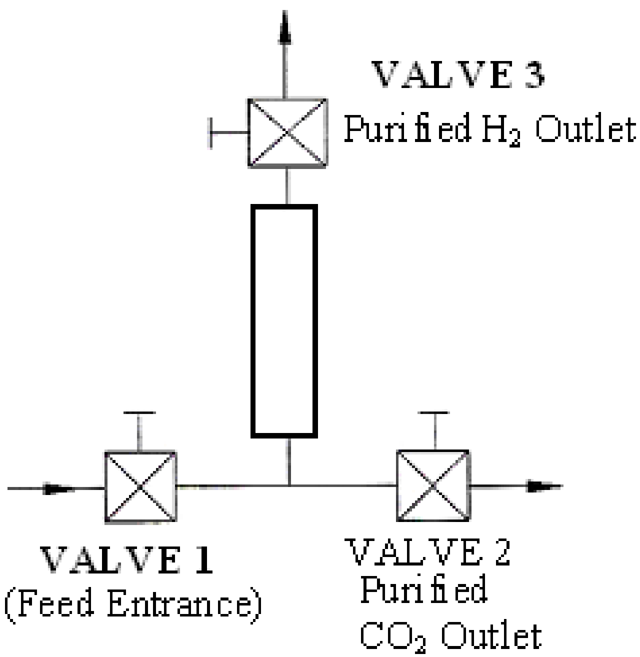
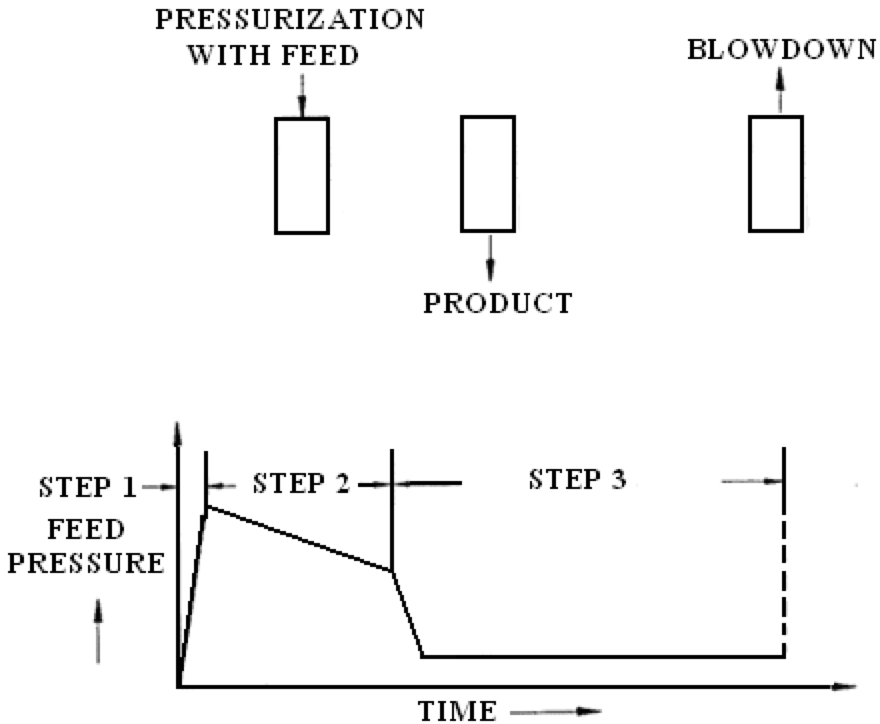
Schematic of the absorber containing ceramic tubules or hollow fibers



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))

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Pressure Swing Absorption (PSAB) in a Membrane Contactor Device

- Basic separation concept implemented with 10% CO_2-90% N_2 gas mixture at 375 kPa and 19.5 wt% aqueous DEA solution (RAPSAB – Rapid Pressure Swing Absorption)

- Its adaptation to the current problem of treating low temperature post-shift reactor synthesis gas at ~20 atm and 150-250^{0}C

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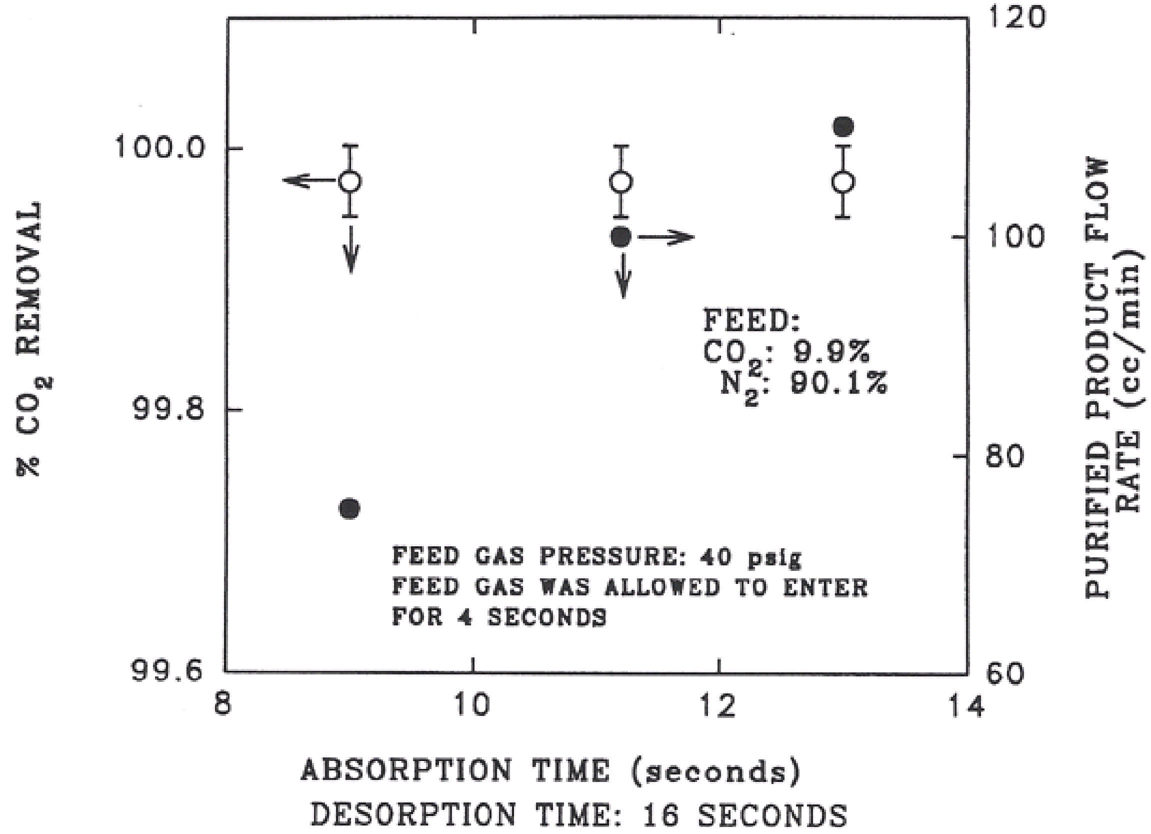
Experimental results for RAPSAB using DEA solution as an absorbent



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

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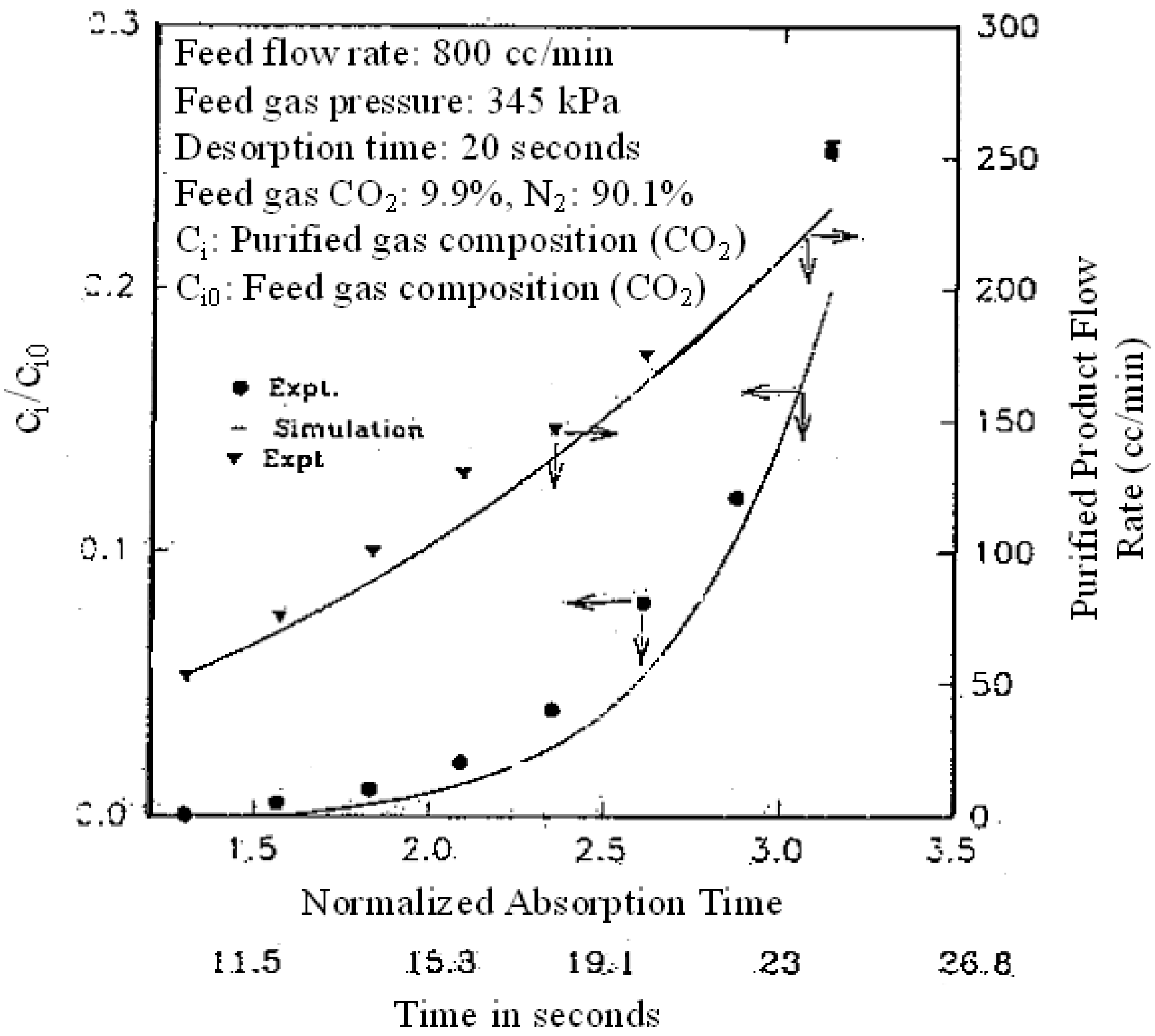
Removal of CO_2 with DEA as an absorbent: experimental results vs. theoretical simulations



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Potential Advantages of the Proposed Separation Technique-1

- Has high solubility selectivity of novel selected liquid absorbents
- 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

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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 1-5 atm

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Nonvolatile Absorbents for PSAB

1.(a) Dendrimers/hyperbranched polymers of lower molecular weight:

Polyamidoamine (PAMAM) generation 0, MW-516, 4 primary amines, 2 tertiary amines;

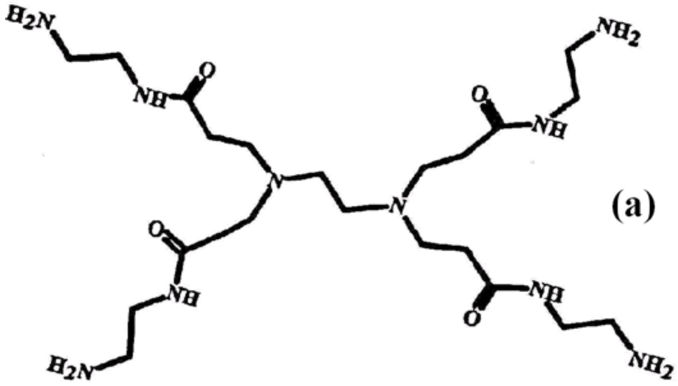
Generation 2, MW-3130

(Dendritech, Midland, MI)

Use in a nonvolatile solvent,

such as polyethylene glycol (PEG 400)

Highly reactive in the presence of moisture



(a) PAMAM dendrimer of generation 0

(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))

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Nonvolatile Absorbents for PSAB

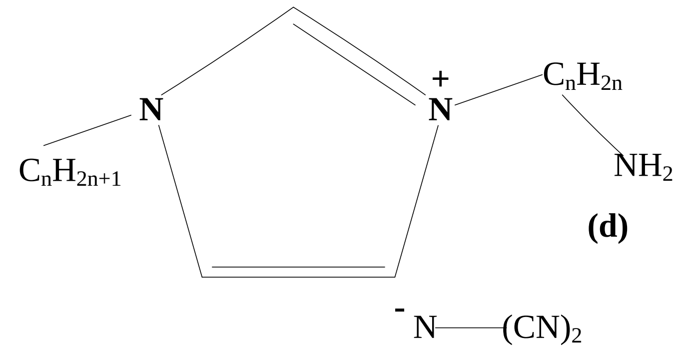
2. Ionic Liquids:

$[bmim]^+[PF_6]^-$ (Fluka)

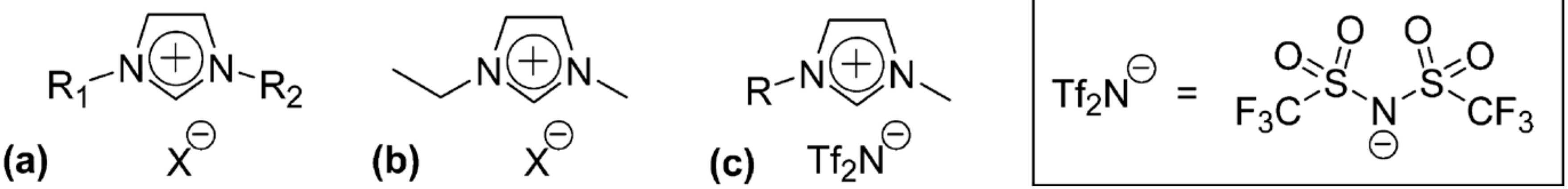
$[bmim]^+[DCA]^-$ (Merck)

$[Am\text{-}Im]^+[DCA]^-$ (Functionalized)

(with or without moisture)



(d) Functionalized IL structure for $[Am\text{-}Im]^+[DCA]^-$



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))

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Adaptation of PSAB to the Current Problem

1. Porous PP membrane substrate replaced by porous PTFE and hydrophobized ceramic tubules (higher temperature, wettability considerations)
2. High pressure means smaller membrane pore size to prevent any phase breakthrough
3. Longer length of hollow fibers in RAPSAB replaced by number of ceramic tubules in series

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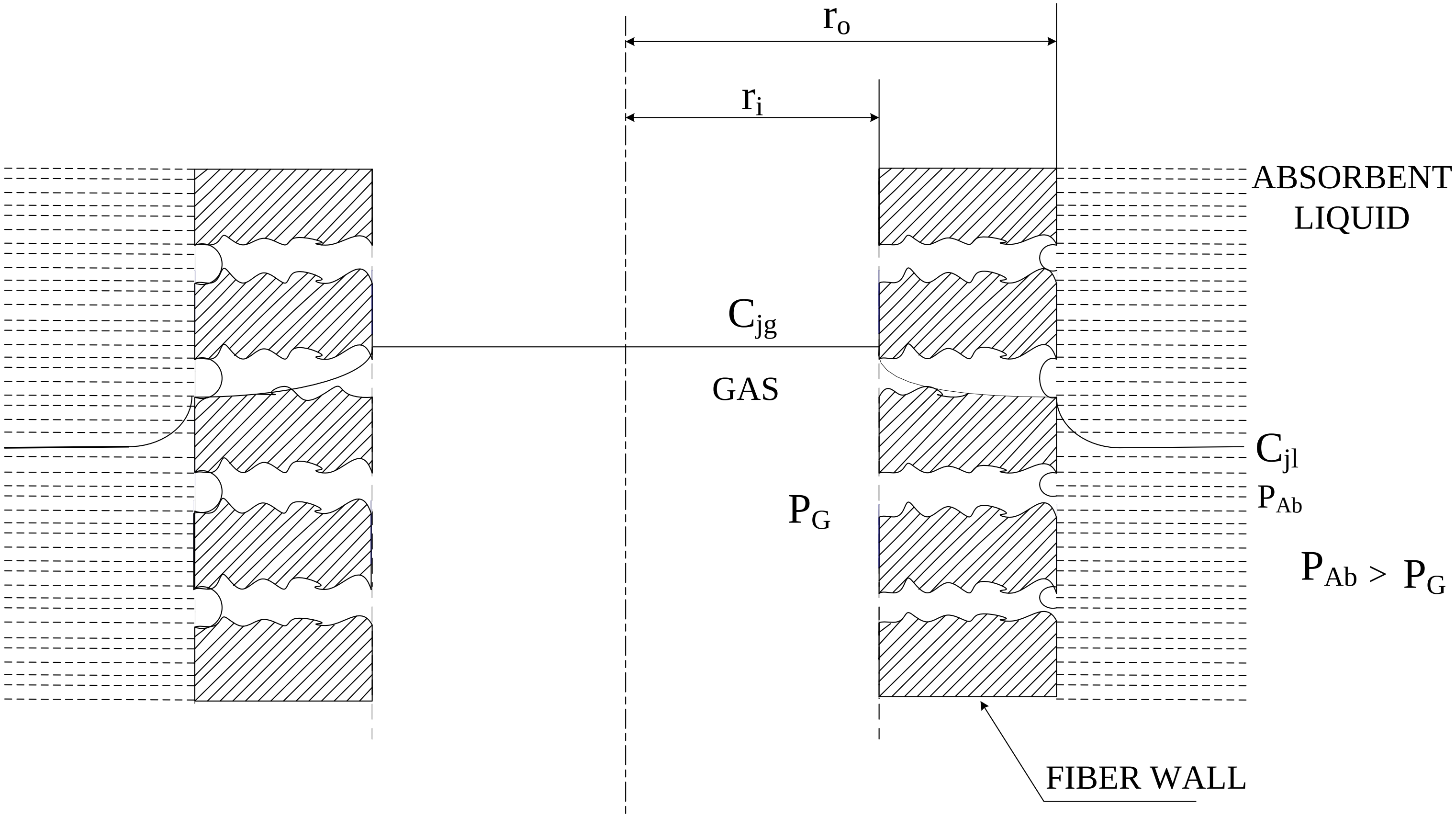
Concentration profile for absorbed species in gas and liquid phases



Breakthrough pressure for a nonwetted pore size of radius r_p (Young-Laplace Equation)

$$\Delta P_{breakthrough} \cong \frac{2\gamma \cos\theta}{r_p}$$

Increase γ, decrease r_p

The pores should remain nonwetted.

Nondisperssive Gas Absorption/Stripping Requires Nonwetted Pores

1. To prevent spontaneous pore wetting

Surface tension of absorbent liquid

$\gamma > \gamma_{critical}$ of the polymeric coating

2. $\gamma_{critical}$ of fluoropolymers, C_{18} surfaces….15-20 dyne/cm
3. Absorbent liquids under consideration have considerably higher γ values; γ will fluctuate due to absorption and desorption of moisture

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Surface Tension / Interfacial Tension

1. $$\gamma = \gamma_{20^0 C} \left(\rho / \rho_{20^0 C} \right)^4$$

   Hasse et al., *J. Chem. Eng. Data*, 54, 2576 (2009).

   [EMIM][MeOHP$_2$] etc.

   Density decreased by about 0.05-0.1 gm/cm^3 over 100^{0}C; density in the range of 1.05-1.35 gm/cm^3

2. Galan Sanchez et al., Trans. I. Chem. E.,Part A, *Chem. Engg. Res. & Dev.*, 85 (A1), 31 (2007)

   →40-45 mN/m for [bmim]$^+$[BF$_4$]$^-$

3. Klomfar et al., *J. Chem. & Engg. Data*, 54, 1389 (2009)
   [C$_n$mim][PF$_6$] → γ decreasing from around 50 mN/m for C$_3$ to 36 mN/m at C$_8$

4. PAMAM dendrimer of generation 0 →55 mN/m at 25^{0}C (Kosaraju et. Al., *I & E C Res.*, 44, 1250 (2005)

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- **Ceramic Tubules:**

  1.5 mm I.D., 3 mm O.D. γ-alumina tubules

  940 m^2/m^3 surface area/device volume

  Pore radius ~0.01μm <0.03μm

  For say, a 40 dyne/cm liquid to withstand 20 atm+, 10 nm pore size with C_{18}-based hydrophobic coatings and epoxy-based tube sheet upto 250^0C

(Media and Process Technology, Pittsburgh, PA; Paul K.T. Liu)

- **Teflon Tubules:**

  0.89 mm I.D., Pore size <0.1μm

  Plasma polymerize a nanoporous fluorosilicone coating to reduce the pore size to ≤0.01μm

(Applied Membrane Technologies, Inc., Minnetonka, MN; Stephen Conover)

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M&P ceramic membrane tubes: 2″ and 4″ commercial elements

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M&P Ceramic Commercial Element

CO_2 Gas-Liquid/Liquid-Gas Mass Transfer Aspects

- Stagnant highly viscous absorbent liquid on the shell side
- Tube-side flowing gas present in pores of membrane

$$Rate\ of\ physical\ gas\ absorption \quad \alpha \quad \sqrt{\frac{D_{CO_2}}{\pi t}}$$

$$Amount\ absorbed\ per\ unit\ area \quad \alpha \quad \sqrt{\frac{D_{CO_2} t}{\pi}}$$

$$D_{CO_2} \quad \alpha \quad \frac{1}{\mu_{absorbent}}$$

- High temperature of operation will reduce $\mu_{absorbent}$ drastically

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Gas Mixture to be Studied

- 45% He, 30% CO_2, Rest being H_2O
- 150-200^{0}C, 200-300 psig
- Helium as a surrogate for H_2

- Typical Gasifier Composition:

  ~38% H_2, 29% CO_2, 33% H_2O, 0.15% CO

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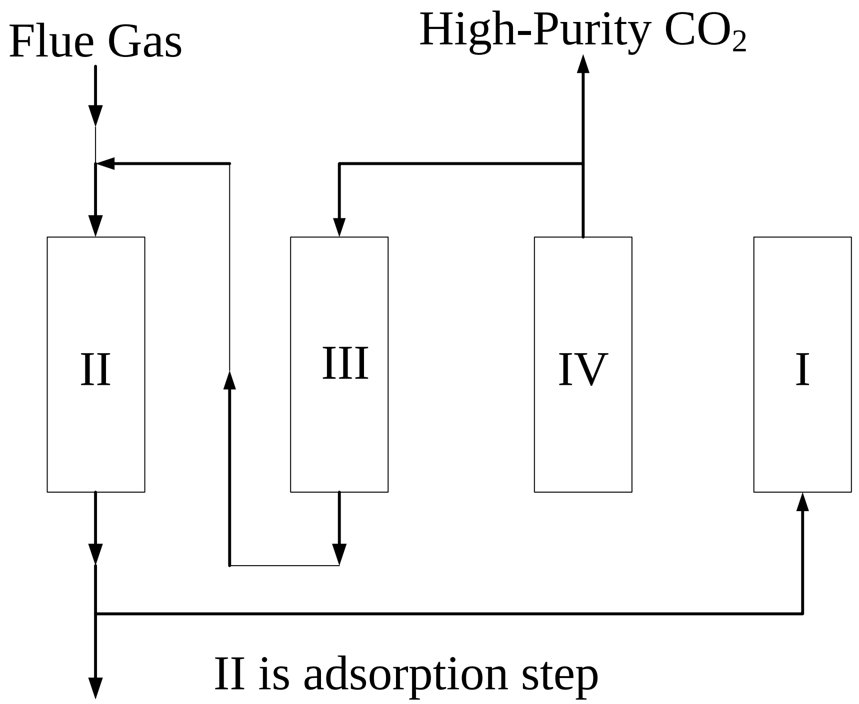
Concentration and Recovery of CO_2 from Flue Gas by Pressure Swing Adsorption



II is adsorption step

III is purge with concentrated CO_2 step

IV is countercurrent blowdown

I is pressurization with adsorption product step

(E.S. Kikkinides, R.T.Yang and S.H.Cho, *Ind. Eng. Chem. Res.*, 32, 2714 (1993))

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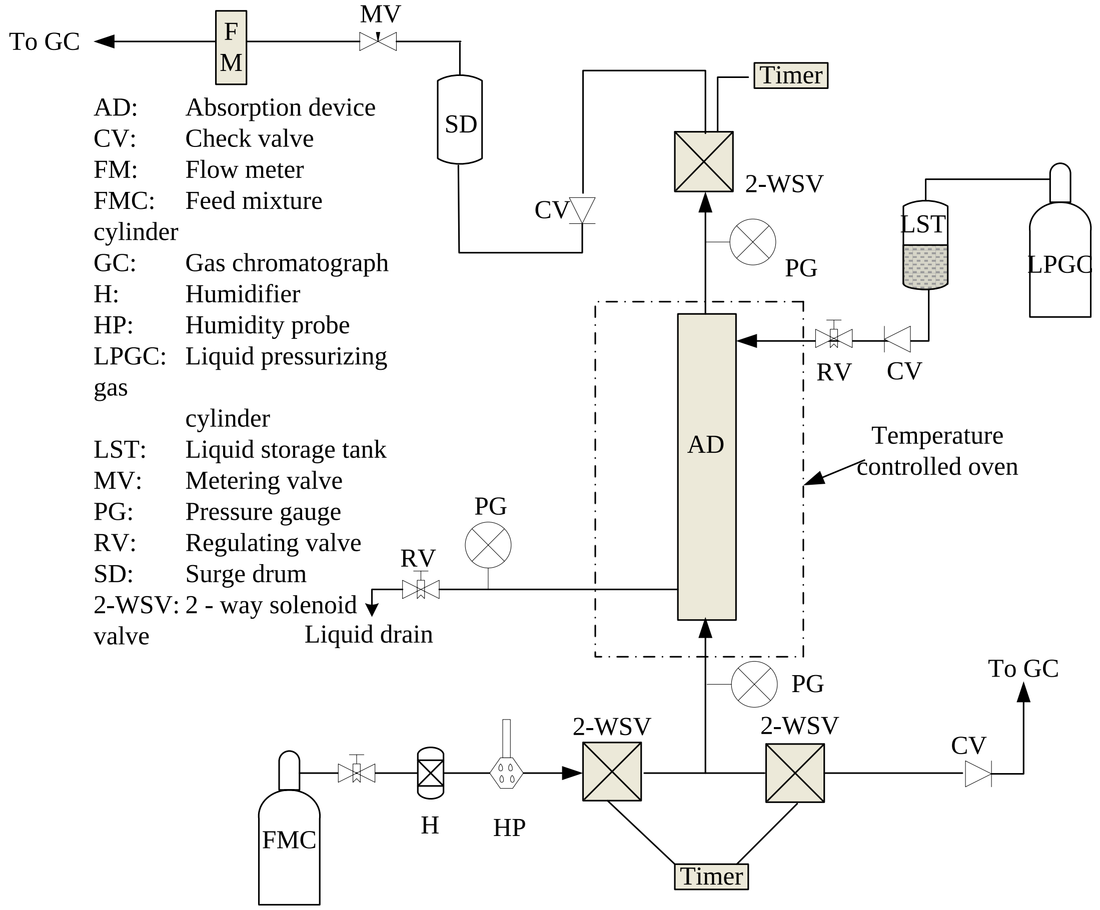
Schematic of the experimental setup for pressure swing absorption



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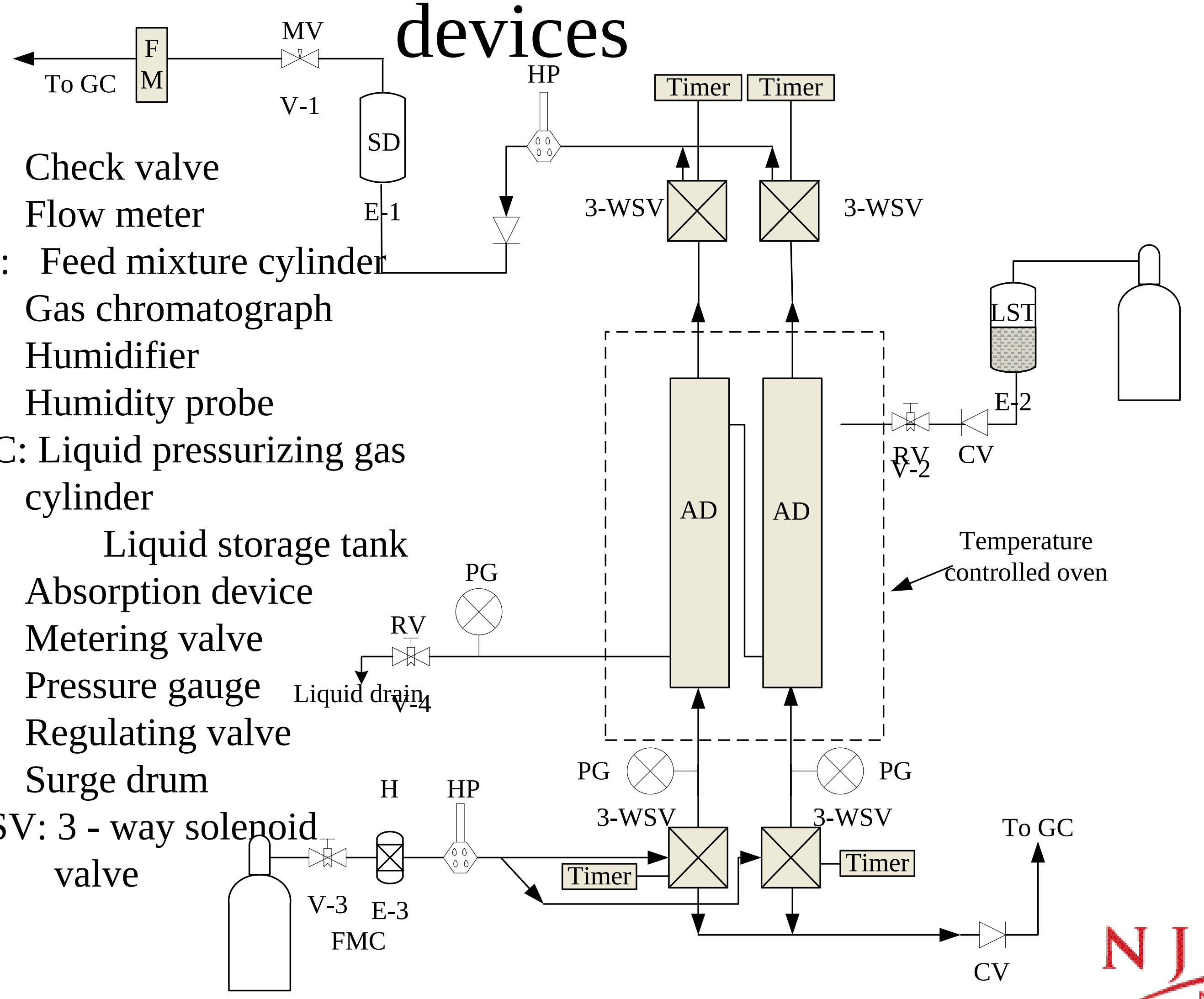
Schematic of the experimental setup for pressure swing absorption using two separate absorption devices

CV: Check valve
FM: Flow meter
FMC: Feed mixture cylinder
GC: Gas chromatograph
H: Humidifier
HP: Humidity probe
LPGC: Liquid pressurizing gas cylinder
LST: Liquid storage tank
AD: Absorption device
MV: Metering valve
PG: Pressure gauge
RV: Regulating valve
SD: Surge drum
3-WSV: 3 - way solenoid valve



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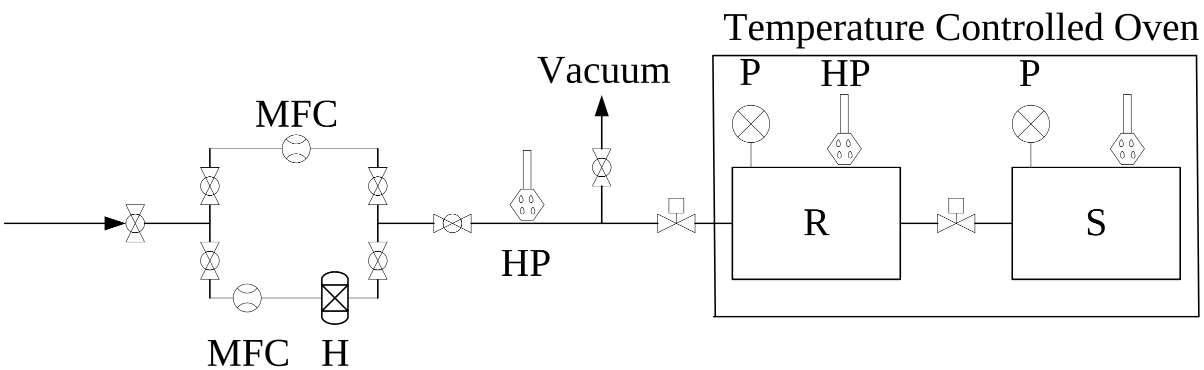
Schematic of the measurement of gas uptake by an absorbent liquid



H Humidifier
HP Humidity probe
MFC Mass flow controller
P Pressure transducer

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Project Objectives

- Develop via laboratory experiments an advanced pressure swing absorption-based device and a cyclic process to produce purified helium (a surrogate for hydrogen) at a high pressure for IGCC-CCS plant’s combustion turbine from low temperature post-shift reactor synthesis gas and simultaneously obtain a highly purified CO_2 stream containing at least 90% of the CO_2 in the post-shift reactor gas stream and suitable for subsequent sequestration

- Provide data and analysis of the cyclic process and device to facilitate subsequent scale up

- Develop a detailed analysis for the process and device to allow economic evaluation for potential larger-scale use

Project Objectives: PHASE-I

I1. Develop an experimental setup for studying the PSAB process

I2. Develop novel gas-liquid absorption modules employing ceramic tubules and polymeric hollow fibers of PTFE

I3. Initiate preliminary studies of pressure swing absorption-based separation of a moist CO_2-He gas mixture at 150-200^{0}C and 200-300 psig simulating a low temperature post-shift reactor synthesis gas stream

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Project Objectives: PHASE-II

II1. Study the performance of the PSAB process for selected absorbents vis-à-vis purification of the feed gas stream to obtain a high pressure purified He stream and a low pressure purified CO_2 stream

II2. Develop experimental setups to measure the solubility and diffusion coefficients of CO_2 and He at the appropriate ranges of temperature and pressure for selected absorbents

II3. Initiate development of a mathematical model of the PSAB device and process

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Project Objectives: PHASE-III

III1. Generate experimental data on the solubility and diffusion coefficient for CO_2 and He for the selected absorbents

III2. Compare the results of simulation of the mathematical model with the observed purification and separation in the PSAB process and device for selected absorbents

III3. Perform simulations of the model to explore scale up of the process to facilitate evaluation of the process

III4. Determine the extent of loss/deterioration of the absorbents over extended periods of operation

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Project Structure

- Project Structure may be described through the List of Tasks describing in detail the following steps
- Design the device and PSAB process after selecting absorbents and the dimensions of the membrane units
- Build the setup
- Perform separation runs
- Analyze the data and focus on conditions showing the desired performance
- Develop a mathematical model for the process
- Determine the solubility and diffusivity of solutes in the absorbent liquids
- Compare model results with experimental data
- Determine absorbent deterioration with time

Tasks to be Performed

- Task 1.0 Project Management and Planning (10/1/09 – 9/30/10)
- Subtask 1.1 Provide quarterly reports at the end of every quarter as well as a Topical Report at the end of year 1 (10/1/09 – 9/30/10)
- Task 2.0 Experimental Program and Technical Activities for Year 1 (10/1/09 – 9/30/10)
- Subtask 2.1: Develop an experimental setup for studying the PSAB device and process (10/1/09 – 5/31/10)
- Subtask 2.2: Develop novel gas-liquid absorption modules (10/1/09 – 6/30/10)
- Subtask 2.3: Initiate preliminary studies of PSAB process (6/1/10 – 9/30/10)

Tasks to be Performed

- Task 3.0 Project Management and Planning (10/1/10 – 9/30/11)
- Subtask 3.1 Provide quarterly reports at the end of every quarter as well as a Topical Report at the end of year 2 (10/1/10 – 9/30/11)
- Task 4.0 Experimental Program and Technical Activities for Year 2 (10/1/10 – 9/30/11)
- Subtask 4.1 Study the performance of PSAB devices and the PSAB process (10/1/10 – 9/30/11)
- Subtask 4.2 Develop experimental setups to measure solubility and diffusion coefficients of CO_2 and He in selected absorbent liquids (10/1/10 – 9/30/11)
- Subtask 4.3 Initiate development of a mathematical model of the PSAB device and process (10/1/10 – 9/30/11)

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Tasks to be Performed

- Task 5.0 Project Management and Planning (10/1/11 – 9/30/12)
- Subtask 5.1 Provide quarterly reports at the end of every quarter as well as the final Project Report at the end of year 3 (10/1/11 – 12/31/12)
- Task 6.0 Experimental Program and Technical Activities for Year 3 (10/1/11-9/30/12)
- Subtask 6.1 Determine the solubility and diffusivity of CO_2 and He in selected absorbents (10/1/11-6/30/12)
- Subtask 6.2 Compare mathematical model simulation results with experimental data from PSAB process (10/1/11-9/30/12)
- Subtask 6.3 Numerically explore scale up of the process to facilitate evaluation of the process (3/1/12-9/30/12)
- Subtask 6.4 Determine the loss/deterioration of the absorbents, especially amines, over extended periods (10/1/11-9/30/12)

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Applicant Name: New Jersey Institute of Technology Award Number: DE-FE0001323

Budget Information - Non Construction Programs

OMB Approval No. 0348-0044

Section A - Budget Summary

Grant Program Function or Activity (a)	Catalog of Federal Domestic Assistance Number (b)	Estimated Unobligated Funds: Federal (c)	Estimated Unobligated Funds: Non-Federal (d)	New or Revised Budget: Federal (e)	New or Revised Budget: Non-Federal (f)	New or Revised Budget: Total (g)
1. Fossil Energy R&D	81.089			$256,239	$82,034	$338,273
2.						$0
3.						$0
4.						$0
5. Totals		$0	$0	$256,239	$82,034	$338,273

Section B - Budget Categories

6. Object Class Categories	Grant Program, Function or Activity (1)	(2)	(3)	(4)	Total (5)
a. Personnel	$0	$0	$92,000	$20,959	$112,959
b. Fringe Benefits	$0	$0	$19,960	$4,257	$24,217
c. Travel	$0	$0	$5,000	$0	$5,000
d. Equipment	$0	$0	$55,000	$24,000	$79,000
e. Supplies	$0	$0	$12,000	$0	$12,000
f. Contractual			$0	$0	$0
g. Construction			$0	$0	$0
h. Other	$0	$0	$3,000	$19,580	$22,580
i. Total Direct Charges (sum of 6a-6h)	$0	$0	$186,960	$68,796	$255,756
j. Indirect Charges	$0	$0	$69,279	$13,238	$82,517
k. **Totals** (sum of 6i-6j)	$0	$0	$256,239	$82,034	$338,273
7. Program Income					$0

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Section C - Non-Federal Resources

(a) Grant Program	(b) Applicant	(c) State	(d) Other Sources	(e) Totals
8.				$0
9.				$0
10.				$0
11.				$0
12. **Total** (sum of lines 8 - 11)	$0	$0	$0	$0

Section D - Forecasted Cash Needs

	Total for 1st Year	1st Quarter	2nd Quarter	3rd Quarter	4th quarter
13. Federal	$256,239	$64,060	$64,060	$64,060	$64,060
14. Non-Federal	$82,034	$20,509	$20,509	$20,509	$20,509
15. **Total** (sum of lines 13 and 14)	$338,273	$84,569	$84,569	$84,569	$84,569

Section E - Budget Estimates of Federal Funds Needed for Balance of the Project

	Future Funding Periods (Years)			
(a) Grant Program	(b) First	(c) Second	(d) Third	(e) Fourth
16. Federal Funds		$261,315	$288,265	$0
17.				
18.				
19.				
20. **Total** (sum of lines 16-19)	$0	$261,315	$288,265	$0

Section F - Other Budget Information

21. Direct Charges	22. Indirect Charges	Modified Total Direct Cost; 316,549 estimated amount of base = $167,032.

23. Remarks

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Project Management Plan

- Project Manager : Prof. Kamalesh K. Sirkar, PI, NJIT
- Post-Doctoral Fellow 1: Dr. Gordana Obuskovic, NJIT
- Post-Doctoral Fellow 2: Dr. Jie Xingming, NJIT
- Graduate Students: Mr. John Chau, NJIT, another to be selected
- Consultant : Dr. Ashok Damle, Techverse Inc., Cary, NC

The Project Manager will interact with the following companies fabricating microporous hollow fiber membranes/tubules:

1. Applied Membrane Technology, Minnetonka, MN (AMT): Stephen Conover, Thomas McEvoy, Dr. Ashok Sharma on porous hollow fiber membranes of Teflon
2. Media & Process Technology, Pittsburgh, PA: Dr. Paul K.T. Liu, Richard Ciora on coating of the surfaces of ceramic tubules of alumina

Activities of PI

- **PI will work with the postdoctoral fellows (PDFs), grad. student and membrane development companies to have the membrane contactors developed**
- **PI will guide the PDFs and grad. student to design the system, order necessary equipment and supplies and have the set up built and tested**
- **PI will supervise the activities of data acquisition, device performance evaluation, estimation of properties and system modeling**
- **PI will lead the activities to take care of DOE reporting requirements and program review meetings**
- **PI will work with consultant to conduct economic evaluation of the process**
- **PI will make presentations and publications of results obtained from the project**

Risk Management

- To prevent leakage of absorbent through microporous PTFE hollow fibers having a plasma polymerized microporous fluorosilicone coating, a finer starting pore size and a provision for leakage collection at the end of tube side

- Capability of the hydrophobic coatings on ceramic tubules to hydrophobize them sufficiently (avoid defects) to eliminate leakage of absorbent into the tube side: make provision for leakage collection at the end of tube-side and a finer starting pore size

- Effect of module diameter and length on He purification ability: smallest possible tubule diameter; increase module length by connecting them in series (oven dimension limitations)

- Achieve a steady state in the cyclic process by preventing a drift in the composition and amount of two purified product streams obtained: balance cycle between absorption and regeneration; fine tune the system

Project Timeline

ID	Task Number	Task Description	Start	Finish	Task #
1	Task 1	Project Management I	10/1/2009	9/30/2010	52.14w
2	SubTask 1.1	Status Report	10/1/2009	9/30/2010	52.14w
3	Task 2	Experimental Program I	10/1/2009	9/30/2010	52.14w
4	Subtask 2.1	Build Experimental Setup	10/1/2009	5/31/2010	34.71w
5	Subtask 2.2	Develop Gas Absorption Modules	10/1/2009	6/30/2010	39w
6	Subtask 2.3	Preliminary Study of PSAB	6/1/2010	9/30/2010	17.43w
7	Task 3	Project Management II	10/1/2010	9/30/2011	52.14w
8	Subtask 3.1	Status Report	10/1/2010	9/30/2011	52.14w
9	Task 4	Technical Program, Year 2	10/1/2010	9/30/2011	52.14w
10	Subtask 4.1	Study PSAB Device and Process	10/1/2010	9/30/2011	52.14w
11	Subtask 4.2	Build Setup for Solubility and Diffusivity	10/1/2010	9/30/2011	52.14w
12	Subtask 4.3	Develop a Model for PSAB Device and Process	10/1/2010	9/30/2011	52.14w
13	Task 5	Project Management III	10/1/2011	9/30/2012	52.29w
14	Subtask 5.1	Status Report	10/1/2011	9/30/2012	52.29w
15	Task 6	Technical Program, Year 3	10/1/2011	9/30/2012	52.29w
16	Subtask 6.1	Measure Solubility and Diffusivity	10/1/2011	6/30/2012	39.14w
17	Subtask 6.2	Simulate Model and Compare	10/1/2011	9/30/2012	52.29w
18	Subtask 6.3	Explore Scale up	3/1/2012	9/30/2012	30.57w
19	Subtask 6.4	Determine Absorbent Loss	10/1/2011	9/30/2012	52.29w

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Milestone Log

PHASE I

- Milestone 1: Novel absorption module fabrication successfully completed (6/30/10)
- Milestone 2: PSAB experimental setup completed (6/30/10)
- Milestone 3: PSAB device appears to function well (9/30/10)

PHASE II

- Milestone 4: PSAB device achieving high purification of He and CO_2 streams (8/31/11)
- Milestone 5: Experimental setups for measuring solubility and diffusivity completed (9/30/11)

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Milestone Log

PHASE III

- Milestone 6: Mathematical Model of PSAB developed (4/30/12)
- Milestone 7: Solubilities and diffusivities of CO_2 and He measured (4/30/12)
- Milestone 8: PSAB process simulated successfully vis-à-vis experimental performance (7/31/12)
- Milestone 9: Absorbent liquid characterized and degradation determined (9/31/12)
- Milestone 10: Scaleup and economic evaluation conducted (9/31/12)

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Closing Comments

- Welcome suggestions from DOE regarding the latest info. on ILs hollow-fiber module shown in Figure 7. The gas or gas mixture is fed inside the fibers and the shell side is filled with an absorbent liquid which does not wet the fibers. The liquid is stationary and its pressure is higher than the gas pressure so that the gas-liquid phase interface is immobilized at each pore mouth on the OD of the microporous membrane (Figure 1). It is assumed that the hollow fibers are arranged in a regular pitch and the analysis based on a single fiber can be extended to the whole device. To this end, we consider the equivalent annulus or free surface model (Happel, 1959) to be valid. This model assumes a cylindrical fluid envelope surrounding each hollow fiber, that is, there exists two concentric cylinders: the inner cylinder consists of one hollow fiber and the outer cylinder consists of the absorbent liquid with a free surface (Figure 10) across which there is no mass transfer. This approximation of Happel's free surface model has been applied successfully to analyzing hollow fiber reverse osmosis systems (Gill and Bansal, 1973).

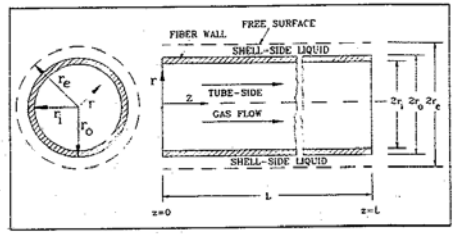

Figure 10. Representation of Happel's free surface model.

Model for water as absorbent

The following assumptions are introduced for absorption of gases into water in the RAPSAB system (steps 1 and 2 in mode 3).

(1) Ideal gas law is valid.

(2) The absorption process is isothermal.

(3) Diffusion and solubility coefficients are constants and independent of concentration.

(4) No reaction takes place between the liquid and any gas component.

(5) The components of the gas phase are in equilibrium with the absorbed components at the gas-liquid interface and Henry's law is valid.

(6) The flow pattern within the fiber bore can be described by the model of plug flow with axial diffusion.

(7) The mass-transfer mechanism from the bulk gas phase to the outside surface of the fiber where the gas-liquid interface is located may be described by a first-order model based upon a constant mass-transfer coefficient and a concentration difference between the two locations.

(8) The pressure drop in the fiber lumen is governed by the Hagen-Poiseuille equation for the compressible fluid without any effect of radial absorption.

(9) The deformation of the fibers due to the higher external pressure of the liquid is negligible so that the fiber size and the void fraction remain unaltered.

(10) End effects are negligible.

(11) Volume of gas in the pores is negligible compared to that in the fiber lumen.

In determining the equivalent radius of free surface, we consider that the relative volume of absorbent liquid surrounding a single fiber is the same as the relative volume of the total liquid surrounding all hollow fibers in the module (Happel, 1959). If ϵ, the void fraction of the fiber bundle, is defined as

$$\epsilon = 1 - \frac{\text{shell-side cross-sectional area occupied by the hollow fibers } (= N\pi r_o^2)}{\text{total cross-sectional area of the shell side } (= \pi r_s^2)}$$

then one can easily obtain:

$$r_e = \left(\frac{1}{1-\epsilon}\right)^{1/2} r_o \tag{1}$$

where r_e is the equivalent radius (Figure 10).
The differential mass balance equation for any species j in a single hollow fiber may be written as (Bhaumik et al., 1994):

$$\frac{\partial C_{jg}}{\partial t} + \frac{\partial [v_g C_{jg}]}{\partial z} + \frac{4K_{jg} d_o}{d_i^2}\left(C_{jg} - C_{jg}^i\right) = D_{jg}\frac{\partial^2 C_{jg}}{\partial z^2} \tag{2}$$

where

$$v_g = -\frac{RTd_i^2}{32\mu_g}\sum_{j=1}^{n}\frac{\partial C_{jg}}{\partial z}; \quad C_{jg}^i = \frac{C_{jl}|_{r=r_o}}{H_j RT} \tag{3}$$

Note that, in writing the balance equation, the ID of the hollow fiber is considered for the convection, diffusion and accumulation terms as the gas flow takes place inside the hollow fiber. However, the mass transfer between the gas and the absorbing liquid actually takes place on the fiber OD, hence the mass-transfer area for the absorption term is based on the OD of the hollow fiber. The boundary conditions and initial condition for any species j (N_2, CO_2) in the gas phase are as follows:

Initial Condition:

$$\text{at } t = 0, C_{jg} = 0 (0 \le z \le L) \tag{4}$$

Boundary Conditions:

$$v_g C_{jg}|_u = v_g C_{jg}|_{z=0} - D_{jg}\left.\frac{\partial C_{jg}}{\partial z}\right|_{z=0} \tag{5a}$$

$$D_{jg}\left.\frac{\partial C_{jg}}{\partial z}\right|_{z=L} = 0 \tag{5b}$$

The corresponding differential equation for the liquid phase balance for species j is:

$$\frac{\partial C_{jl}}{\partial t} = D_{jl}\left(\frac{\partial^2 C_{jl}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{jl}}{\partial r}\right) \tag{6}$$

Due to cylindrical symmetry, we have ignored any diffusion in the θ direction. The initial and boundary conditions are:

Initial Condition:

$$\text{at} \quad t=0,\ C_{jl}=0 (0 \le z \le L \quad \text{and} \quad r_o < r < r_e) \tag{7}$$

Boundary Conditions:

$$-D_{jl}\frac{\partial C_{jl}}{\partial r}\bigg|_{r=r_o} = K_{jg}\left(C_{jg} - \frac{C_{jl}|_{r=r_o}}{H_j RT}\right) \tag{8a}$$

$$\frac{\partial C_{jl}}{\partial r}\bigg|_{r=r_e} = 0 \tag{8b}$$

There are a variety of methods such as finite difference, orthogonal collocation, and method of lines available for the numerical solution of PDEs in time and spatial dimensions. We have adopted here the method of lines technique in which only the spatial gradients are discretized by finite difference equations thus reducing the system of PDEs to a coupled system of ODEs in the time domain (Brian et al., 1987). Following Brian et al. (1987), the effective absorption column length in the axial direction and the annular section between the fiber outside radius $[r = r_o \Rightarrow \eta = (r/r_e) = a]$ and the free surface radius $(r = r_e \Rightarrow \eta = 1)$ in the radial direction have been discretized into NB and NR points, respectively. The normalized distance between any two adjacent axial point is ΔX where $X = z/L$ (L being the module length) and that between two radial points is $\Delta\eta$. The procedure has transformed the nondimensional forms of Eqs. 2 and 6 for a single species to [NB + NB X NR] ordinary differential equations in normalized time parameter (Bhaumik et al., 1994).

Model development for a reactive system

Aqueous solution of diethanolamine (DEA) reacts reversibly with CO_2. Sada et al. (1985) proposed the following reaction scheme for CO_2 absorption in an aqueous DEA solution:

$$CO_2 + R_2NH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R_2NH^+COO^- \tag{9}$$

$$R_2NH + R_2NH^+COO^- \overset{k_3}{\rightarrow} R_2NH_2{}^+ + R_2NCOO^- \tag{10}$$

The mechanism proposed has two steps: formation of zwitterion followed by the removal of a proton by amine. If steady-state approximation is applied to the unstable intermediates, then a homogeneous reaction rate (Sada et al., 1985) can be expressed as

$$r_{CO_2} = \frac{[R_2NH][CO_2]}{\dfrac{1}{k_1} + \dfrac{k_2}{k_1 k_3 [R_2NH]}} \tag{11}$$

If the first term in the denominator is much smaller than the second term, the reaction becomes second order with respect to amine and the rate constant becomes k_1k_3/k_2. On the other hand, if the first term is much larger than the second, the reaction will be first-order with respect to amine and the overall order will be second where the rate constant would be k_1.

For this initial study, the reaction mechanism and the reaction rate expression proposed by Sada et al. (1985) are being considered and a simplified model for gas absorption in mode 3 has been developed using Happel's (1959) free surface model (guided by the modeling and results of Karoor, 1992). One fiber surrounded by reactive absorbents is considered in a unit cell of radius r_e. Gas flows through the fiber lumen. Gas pressure drop in the fiber lumen was also included in the model. The governing balance equations and boundary conditions for any species j (N_2, CO_2) in the gas phase continue to be Eqs. 2, 3, 4, 5a and 5b.

In the liquid phase, now, there are at least three components to be considered: N_2, CO_2, and the amine. For N_2, the mass balance and initial and boundary conditions are:

$$\frac{\partial C_{N_2l}}{\partial t} = D_{N_2l}\left(\frac{\partial^2 C_{N_2l}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{N_2l}}{\partial r}\right) \tag{12}$$

Initial Condition:

$$\text{at} \quad t=0, \quad C_{N_2l}=0\ (0 \le z \le L \quad \text{and} \quad r_o < r < r_e) \tag{13}$$

Boundary Conditions:

$$-D_{N_2l}\frac{\partial C_{N_2l}}{\partial r}\bigg|_{r=r_o} = K_{N_2g}\left(C_{N_2g} - \frac{C_{N_2l}|_{r=r_o}}{H_{N_2}RT}\right) \tag{14}$$

$$\frac{\partial C_{N_2l}}{\partial r}\bigg|_{r=r_e} = 0 \tag{15}$$

The mass balance equation and the initial and boundary conditions for CO_2 (represented by A) in the liquid phase are:

$$\frac{\partial C_{Al}}{\partial t} = D_{Al}\left(\frac{\partial^2 C_{Al}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{Al}}{\partial r}\right) - \frac{C_{Al}C_{Bl}}{\dfrac{1}{k_1} + \dfrac{k_2}{k_1k_3C_{Bl}}} \tag{16}$$

where diethanolamine has been represented as B.

Initial Condition:

$$C_{Al}(z, r, t=0) = 0 \tag{17}$$

Boundary Conditions:

$$-D_{Al}\frac{\partial C_{Al}}{\partial r}\bigg|_{r=r_o} = K_{Ag}\left(C_{Ag} - \frac{C_{Al}|_{r=r_o}}{H_A RT}\right) \quad (18)$$

$$\frac{\partial C_{Al}}{\partial r}\bigg|_{r=r_c} = 0 \quad (19)$$

The mass balance equation with the initial and boundary conditions for DEA are

$$\frac{\partial C_{Bl}}{\partial t} = D_{Bl}\left(\frac{\partial^2 C_{Bl}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{Bl}}{\partial r}\right) - \frac{2\, C_{Al}\, C_{Bl}}{\dfrac{1}{k_1} + \dfrac{k_2}{k_1 k_3 C_{Bl}}} \quad (20)$$

Initial Condition:

$$C_{Bl}(z,r,t=0) = C_{Bl0} \quad (21)$$

Boundary Conditions:

$$\frac{\partial C_{Bl}}{\partial r}\bigg|_{r=r_o} = 0 \quad (22)$$

$$\frac{\partial C_{Bl}}{\partial r}\bigg|_{r=r_c} = 0 \quad (23)$$

Partial differential Eqs. 2, 12, 16, and 20 are to be solved simultaneously along with the corresponding initial and boundary conditions identified above. They were solved in dimensionless form using the method of lines technique to convert the partial differential equations (PDEs) into ordinary differential equations (ODEs) in time and spatial dimensions. The computer codes were written in Fortran 77 using the IMSL subroutine, DIVPAG; the program was run in the mainframe computer, VAX/VMS environment.

Results and Discussion

A large number of preliminary experiments were carried out with water as the stationary absorbent for absorption of CO_2 from a N_2-CO_2 gas mixture. This allowed the development of the cycles and evaluation of the comparative performance of the cycles. Afterwards, fewer experiments were carried out using 19.5% solution of DEA in water as the absorbent. The steady-state purification results will be presented and discussed first for water and then for the reactive DEA solution. Two items, namely, the extent of purification of the feed gas and the production rate of this high-pressure feed gas are of interest. Although the production rate and quality of the CO_2-rich stream obtained via vacuum desorption are also of interest, these aspects are not being covered here due to the nature of the RAPSAB cycles studied.

Water absorbent in modes 2 and 3

Experiments have been carried out in modes 2 and 3 with water as the absorbent by varying the time for the absorption part of the cycle. The desorption time was maintained always at 15 s since earlier studies indicated this to be the shortest time needed for effective desorption. The feed gas mixture contained either 10.2% or 9.9% CO_2, the balance being N_2. Modules 4 and 5 were used for mode 3 type of operation; only module 5 was used for mode 2 type of operation. The time duration for absorption and desorption part of the simple cycle in mode 3, the feed flow rate, and the purified product flow rate for all experiments are identified in Table 2 along with the purified gas composition in each case. The feed gas flow rate was kept constant for any given module as the absorption time was changed. One observes that as the absorption time increases the purified product gas flow rate increases; simultaneously, the CO_2 content of the purified outlet product gas increases signifying lower levels of purification. For module 4, an absorption time of 10 s yielded the best product quality, such as 2.5% CO_2. Whereas for module 5, which has a much larger surface area per unit volume, the same length of absorption time achieved a much lower CO_2 composition (1.48%).

The experimental data obtained with module 5 in mode 3 operation have been compared with the numerical model simulation results. They are identified in Figure 11. Normalized high-pressure exit compositions have been plotted against the normalized absorption time ($D_{1l}t/r_c^2$). The experimental values of the purified gas flow rate for different nor-

Table 2. Experimental Results for Water Absorbent Using Modules 4 and 5 in Mode 3

Exp. No.	Module No.	Abs. Time (s)	Des. Time (s)	Feed Flow Rate (cm^3/min)	Feed Pres. (kPa)	Product Outlet Comp.*	Product Flow Rate (cm^3/min)
7-1	4	10	15	150	135 ~ 170	CO_2: 2.50%	~ 5
7-2	4	13	15	150	170 ~ 205	CO_2: 2.68%	~ 8
7-3	4	16	15	150	~ 205	CO_2: 2.95%	~ 18
7-4	4	20	15	150	205 ~ 240	CO_2: 3.12%	~ 25
7-5	5	10	15	120	~ 135	CO_2: 1.48%	~ 5
7-6	5	12	15	120	~ 170	CO_2: 1.82%	~ 10
7-7	5	15	15	120	~ 205	CO_2: 2.39%	~ 15
7-8	5	18	15	120	~ 240	CO_2: 2.85%	~ 22
7-9	5	19.5	15	120	~ 275	CO_2: 3.42%	~ 32
7-10	5	21	15	120	~ 310	CO_2: 4.55%	~ 40
7-11	5	22.5	15	120	~ 310	CO_2: 5.64%	~ 50
7-12	5	25	15	120	~ 310	CO_2: 6.90%	~ 60

Feed Composition: 10.2% CO_2-Balance N_2
* Balance N_2

M&P Ceramic Tubes and 4-inch Commercial Element

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