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DOE/PC/90300--T9

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JUL 28 1993

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TECHNICAL PROGRESS REPORT

CONTRACT TITLE: Rapid Pressure Swing Absorption Cleanup of Post-Shift
Reactor Synthesis Gas

CONTRACT NUMBER: DE-FG22-90PC90300

CONTRACT PERIOD: 9/7/90 - 8/31/93

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REPORT NUMBER: 9

REPORT PERIOD: 11/1/92 - 1/31/93

REPORTING DATE: April 30, 1993

PREVIOUS REPORT DATE: January 29, 1993

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Overview of Progress

A number of experiments were carried out using a reactive absorbent such as 19.5 % aqueous solution of diethanolamine (DEA) for the absorption of CO_2 from a CO_2 - N_2 feed gas mixture. A set of experiments were reported in our last Technical Progress Report (Report No. 8) for the same system at a feed gas pressure of about 25 psig. In the set of experiments reported here, the flow rate of feed gas mixture was increased to achieve a substantially higher gas pressure in the fiber lumen which would enhance the CO_2 absorption characteristics as higher pressure increases the rate of absorption. Some of these experiments were carried out using the Mode 3 type of operation and some with the Mode 2 type of operation. Module No. 5 was used in all experiments. The details of the module are given in Technical Progress Report No. 7. A feed gas mixture of 9.9% CO_2 and balance N_2 was used in all experiments.

We have initiated the development of a theoretical model for the absorption part of the RAPSAB cycle (Mode 3) where the reactive absorbent (DEA) is used in an aqueous solution to remove CO_2 from a CO_2 - N_2 mixture.

Theoretical Model Development for a Reactive System

Aqueous solution of diethanolamine (DEA) reacts reversibly with CO_2 . Several investigators have proposed various reaction schemes. Danckwerts and Sharma (1966) proposed the following reaction scheme for CO_2 absorption in an aqueous DEA solution:

where DEA is represented as R_2NH . The reaction is second order and the rate of reaction is expressed by

$$\text{Rate of reaction} = k_{Am} [R_2NH] [CO_2] \quad (2)$$

where k_{Am} is the second order rate constant for the amine.

Hikita et al. (1980) proposed the formation of a dimer of DEA, followed by the formation of a carbamate which then ionizes:

Equation (4) is the rate limiting step.

Sada et al. (1985) proposed the following reaction scheme:

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

$$r_{CO_2} = \frac{[R_2NH][CO_2]}{\frac{1}{k_1} + \frac{k_2}{k_1 k_3 [R_2NH]}} \quad (8)$$

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 $k_1 k_3 / k_2$. 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 the 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 (1958) free surface model. One fiber is considered in a unit cell of radius r_e (Figure 1) surrounded by reactive absorbents. 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 are given below:

$$\frac{\partial C_{jg}}{\partial t} = D_{jg} \frac{\partial^2 C_{jg}}{\partial z^2} - \frac{\partial}{\partial z} (v_z C_{jg}) - \frac{4K_{jg} d_o}{d_i^2} (C_{jg} - C_{jg}^i) \quad (9)$$

$$\text{where} \quad C_{jg}^i = \frac{C_{jl}|_{r=r_e}}{H_j RT} \quad \text{and} \quad v_z = -\frac{RT d_i^2}{32 \mu_g} \sum_{j=1}^n \frac{\partial C_{jg}}{\partial z} \quad (10)$$

$$\text{Initial Condition:} \quad \text{at } t = 0, C_{jg} = 0 \quad (0 < z < L) \quad (11)$$

Boundary conditions:

$$v_z C_{jg}|_u = v_z C_{jg}|_{z=0} - \dot{D}_{jg} \frac{\partial C_{jg}}{\partial z} \Big|_{z=0} \quad (12); \quad -D_{jg} \frac{\partial C_{jg}}{\partial z} \Big|_{z=L} = 0 \quad (13)$$

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

$$\frac{\partial C_{N_2l}}{\partial t} = D_{N_2l} \left[\frac{\partial^2 C_{N_2l}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{N_2l}}{\partial r} \right] \quad (14)$$

$$\text{Initial condition: at } t = 0, C_{N_2l} = 0 \quad (0 < z < L \text{ and } r_0 < r < r_e) \quad (15)$$

Boundary Conditions:

$$-D_{N_2l} \frac{\partial C_{N_2l}}{\partial r} \Big|_{r=r_o} = K_{N_2g} \left[C_{N_2g} - \frac{C_{N_2l}|_{r=r_o}}{H_{N_2} RT} \right] \quad (16); \quad \frac{\partial C_{N_2l}}{\partial r} \Big|_{r=r_e} = 0 \quad (17)$$

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

$$\frac{\partial C_{Al}}{\partial t} = D_{Al} \left[\frac{\partial^2 C_{Al}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{Al}}{\partial r} \right] - \frac{C_{Al} C_{Bl}}{\frac{1}{k_1} + \frac{k_2}{k_1 k_3 C_{Bl}}} \quad (18)$$

where diethanolamine has been represented as B.

$$\text{Initial Condition: } C_{Al}(z, r, t = 0) = 0 \quad (19)$$

Boundary Conditions:

$$-D_{Al} \frac{\partial C_{Al}}{\partial r} \Big|_{r=r_o} = K_{Ag} \left[C_{Ag} - \frac{C_{Al}|_{r=r_o}}{H_A RT} \right] \quad (20); \quad \frac{\partial C_{Al}}{\partial r} \Big|_{r=r_e} = 0 \quad (21)$$

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

$$\frac{\partial C_{Bl}}{\partial t} = D_{Bl} \left[\frac{\partial^2 C_{Bl}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{Bl}}{\partial r} \right] - \frac{2 C_{Al} C_{Bl}}{\frac{1}{k_1} + \frac{k_2}{k_1 k_3 C_{Bl}}} \quad (22)$$

$$\text{Initial condition: } C_{Bl}(z, r, t = 0) = C_{Bl0} \quad (23)$$

Boundary conditions:

$$\frac{\partial C_{Bl}}{\partial r} \Big|_{r=r_o} = 0 \quad (24); \quad \frac{\partial C_{Bl}}{\partial r} \Big|_{r=r_e} = 0 \quad (25)$$

Partial differential equations (9), (14), (18), and (22) are to be solved simultaneously along with the corresponding initial and boundary conditions identified above. The details of the solution procedure and the results will be given in our next report.

Experimental Details

A number of experiments were carried out using Mode 3 as well as Mode 2 type of operation for the absorption of CO₂ from a CO₂ - N₂ mixture using a 19.5% aqueous solution of diethanolamine (DEA) as an absorbent. Experimental procedures for Mode

3 and Mode 2 type of operation were described in our last report (Technical Progress Report No. 8). A number of experiments using Mode 3 type of operation were reported in Technical Progress Report No. 8 for the absorption of CO_2 from a CO_2 - N_2 mixture with 19.5% aqueous solution of diethanolamine (DEA) as an absorbent. In the present set of experiments, the volumetric flow rate of feed gas mixture was increased substantially to raise the feed gas pressure in the fiber lumen. Also a number of experiments using Mode 2 type of operation were carried out for the absorption of CO_2 from a CO_2 - N_2 mixture with 19.5% aqueous solution of diethanolamine (DEA) as an absorbent.

Results and Discussion

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 1 along with the purified gas composition in each case. The feed gas flow rate was kept constant at 700 cc/min as the absorption time was changed. Module No. 5 and a CO_2 - N_2 mixture of 9.9% CO_2 and balance N_2 were used for all experiments: a 19.5% diethanolamine (DEA) solution in water was used as the absorbent. It was observed that at this inlet feed flow rate, there was no CO_2 in the purified gas stream up to a certain length of time for different absorption times when desorption time was kept constant at 16 seconds. This simultaneous absorption and desorption constitute a complete cycle for this particular mode of operation. The system was run for 8 hours for each value of absorption time, e.g., 10, 12, 14, and 16 seconds. Initially, there was no CO_2 in the

purified stream for each such run, but for experiments 9.1-3 and 9.1-4 it was observed that after 5 (for experiment no. 9.1-3) and 3 (for experiment no. 9.1-4) hours, CO₂ showed up in the purified stream and after that concentration of CO₂ continuously increased in the purified stream. Initially, therefore, in each run there was no CO₂ in the purified stream, but after certain time it appeared. The time, during which there was no CO₂ in the purified stream, is identified as stability time in Table 1. If we compare the product flow rate results with our previous results at 25 psig as reported in our last progress report (Technical Progress Report No. 8), we find that higher pressure has enhanced the absorption behavior of CO₂ as shown by the increase in N₂ production rate. Experiments 9.1-3 and 9.1-4 were not stable for long periods since the desorption time was not enough to pull all CO₂ from the liquid phase; with time the DEA solution became saturated. We are now exploring the solution of this problem by increasing the desorption time. We also have to carry out first two experiments (9.1-1, 9.1-2) for longer time to see how long it remains stable.

For different experimental runs in the Mode 2 type of operation, the duration of the open and close settings of the solenoid valves and the corresponding valves of the feed gas pressure have been identified in Table 2. The purification results of each such run identified in Table 2 are provided in Table 3. In these set of experiments, the metering valve was set at 1500 cc/min and the feed gas mixture was allowed to enter the module for 4 seconds; the purified gas was taken out for different times. A CO₂ - N₂ mixture of 9.9% CO₂ and balance N₂ was used for all experiments and 19.5% diethanolamine (DEA)

solution was used as the absorbent. For these set of experiments, desorption side gas mixture was also analyzed and the desorbed gas flow rates are also identified in Table 3. If we compare these results with the results obtained from Mode 3 type of operation, it could be concluded that Mode 2 type of operation is better than the Mode 3 type of operation on the basis of production rate as well as stability.

Notation

C_{Al}	= concentration of species A in the liquid phase, mol/m ³
C_{Bl}	= concentration of species B in the liquid phase, mol/m ³
C_{BIO}	= initial concentration of species B in the liquid phase, mol/m ³
C_{jg}	= concentration of species j in the gas phase, mol/m ³
C_{N_2g}	= concentration of N ₂ in the gas phase, mol/m ³
D_{Al}	= diffusion coefficient of species A in the liquid phase, m ² /s
D_{Bl}	= diffusion coefficient of species B in the liquid phase, m ² /s
D_{jg}	= diffusion coefficient of species j in the gas phase, m ² /s
D_{N_2l}	= diffusion coefficient of N ₂ in the liquid phase, m ² /s
d_i	= inside diameter of a hollow fiber, m
d_o	= outside diameter of a hollow fiber, m
H_A	= solubility coefficient of gas species A in a liquid, mol/(m ³ .Pa)
H_j	= solubility coefficient of gas species j in a liquid, mol/(m ³ .Pa)
H_{N_2}	= solubility coefficient of gas N ₂ in a liquid, mol/(m ³ .Pa)
K_{Ag}	= gas side mass transfer coefficient of species A, m/s
K_{jg}	= gas side mass transfer coefficient of species j, m/s
k_{Am}	= second order rate constant for the amine
k_1	= rate constant for CO ₂ reaction in DEA solution, m ³ /(mol.s)
k_2, k_3	= rate constant for CO ₂ reaction in DEA solution
L	= effective fiber length in a module, m
R	= universal gas constant, (m ³ .Pa)/(mol.°K)

r = radial distance, m
 r_e = equivalent radius of free surface, m
 r_i = inside radius of a hollow fiber, m
 r_o = outside radius of a hollow fiber, m
 T = temperature, °K
 t = time, s
 v_z = gas velocity in fiber lumen, m/s
 z = longitudinal distance, m

Greek

μ = viscosity, Pa.s

Superscript

i = interface

Subscript

g = gas phase

j = component j

l = liquid phase

u = upstream section of the hollow fiber module

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**Table 2: Duration of Different Settings of Solenoid Valves
for Mode 2 Operation with Aqueous DEA Solution⁺ as an Absorbent**

Experiment No.	Module No.	Mode of Operation	Pressure in fiber lumen (psig)	Valve # 1*		Valve # 3*		Valve # 2*		Total Cycle Time (Seconds)
				Open (Seconds)	Close (Seconds)	Close (Seconds)	Open (Seconds)	Close (Seconds)	Open (Seconds)	
9.2-1	5	2	40	4	25	4	5	9	16	25
9.2-2	5	2	40	4	27.2	4	7.2	11.2	16	27.2
9.2-3	5	2	40	4	29	4	9	13	16	29

+ 19.5% DEA in water

* valves refer to Figure 2.

Table 3: Experimental Results for RAPSAB using DEA Solution⁺ as an Absorbent
and Mode 2 of Operation

Experiment No.	Module No.	Mode of Operation	Feed Pressure (psig)	Purified Gas Composition*	Stability (hours)	Purified Product Gas Flow Rate (cc/min)	Desorbed Gas Composition*	Desorbed Gas Flow Rate (cc/min)
9.2-1 ^{***}	5	2	40	CO ₂ : 0.0%	at least 7	~75	CO ₂ : 15.0%	145
9.2-2	5	2	40	CO ₂ : 0.0%	at least 7	~100	CO ₂ : 18.5%	120
9.2-3	5	2	40	CO ₂ : 0.0%	at least 7	~110	CO ₂ : 20.0%	110

+ 19.5% DEA in water

* Balance N₂

** For valve settings, see Table 1.

*** Feed metering valve set at 1500 cc/min.

Table 1. Experimental Results for RAPSAB using DEA Solution⁺,
Mode 3 Type of Operation and a Higher Feed Pressure of 40 psig

Experiment No.	Module No.	Absorption Time (Seconds)	Desorption Time (Seconds)	Feed Flow Rate (cc/min)	Feed Pressure (psig)	Product Outlet Composition*	Stability Time (hours)	Product Flow Rate (cc/min)
9.1-1	5	10	16	700	40	CO ₂ : 0.0%	at least 8	~50
9.1-2	5	12	16	700	40	CO ₂ : 0.0%	at least 8	~80
9.1-3	5	14	16	700	40	CO ₂ : 0.0%	5	~105
9.1-4	5	16	16	700	40	CO ₂ : 0.0%	3	~140

+ 19.5% DEA in water
Feed Composition: CO₂:9.9%, N₂: 90.1%
* Balance N₂

Figure 1. Concentration profile for absorbed species in gas and liquid phases

Figure 2. Solenoid valve locations in RAPSAB apparatus for Mode 2

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