CO₂ Capture by Absorption with Potassium Carbonate

Quarterly Progress Report

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Abstract

The objective of this work is to improve the process for CO₂ capture by alkanolamine absorption/stripping by developing an alternative solvent, aqueous K₂CO₃ promoted by piperazine. A rigorous thermodynamic model has been further developed with a stand-alone FORTRAN code to represent the CO₂ vapor pressure and speciation of the new solvent. Gas chromatography has been used to measure the oxidative degradation of piperazine. The heat exchangers for the pilot plant have been received. The modifications are on schedule for start-up in November 2003.

Contents

Disclaimer	2
Abstract	3
List of Figures	5
List of Tables	6
Introduction	7
Experimental	7
Results and Discussion	7
Conclusions	8
Future Work	8
Task 1 – Modeling Performance of Absorption/Stripping of CO ₂ with Aqueous K ₂ CO ₃ Promoted by Piperazine.....	9
Subtask 1.1a – Modify Vapor-Liquid Equilibrium (VLE) Model – Stand-alone FORTRAN Model	9
Introduction	9
Experimental (Equilibrium Modeling)	9
Results and Discussion	11
Conclusions	14
Subtask 1.1b – Modify Vapor-Liquid Equilibrium (VLE) Model – Aspen Plus	17
Introduction	17
Experimental (Equilibrium Methods)	17
Results and Discussion	19
Conclusions	22
Future Work	22
Subtask 1.3 – Develop Integrated Absorber/Stripper Model – ACM Model for Stripper.....	23
Introduction	23
Experimental.....	23
Results and Discussion – Work in Progress	29
Conclusions – Proposed Work for the Next Quarter	30
Task 2 – Pilot Plant Testing	30
Subtask 2.1 – Pilot Plant Test Plan – Development of Analytical Methods	31
Introduction	31
Experimental.....	31
Results and Discussion	33
Conclusions	35
Future Work	36
Subtask 2.2 – Design, Modifications, Order Equipment and Packing Materials	37
Project Management	37
Experimental.....	37
Results and Discussion	43
Conclusions	48
References	51

Figures

- Figure 1 Electrolyte NRTL Model Predictions of CO₂ Vapor Pressure in Aqueous Potassium Carbonate Solutions (16) Using Parameters Shown in Table 1
- Figure 2 Speciation in 0.6 m PZ at 333 K
- Figure 3 Speciation in 3.6 m K⁺/0.6 m PZ at 333 K
- Figure 4 CO₂ Solubility in Aqueous PZ Solutions at 25 and 40°C
- Figure 5 CO₂ Solubility of K₂CO₃, KHCO₃, and PZ Mixtures at 25°C
- Figure 6 VLE of PZ Species in Aqueous K⁺/PZ at constant loading of 1 m of CO₂
- Figure 7 VLE Species in Aqueous K⁺/PZ at constant loading of 1 m of CO₂
- Figure 8 VLE of PZ Species in Aqueous K⁺/PZ at 60°C
- Figure 9 VLE Species in Aqueous K⁺/PZ at 60°C
- Figure 10 Gas Chromatogram for Long Column Amine Calibration
- Figure 11 Gas Chromatogram for Short Column Amine Calibration
- Figure 12 Piperazine Loss for 5.0/2.5 Solutions
- Figure 13 Entrainment Calculated for 5.0/2.5 Experiments
- Figure 14 Gantt Chart for CO₂ Removal Project
- Figure 15 Absorber Penetration Locations (TE)
- Figure 16 Stream Designations

Tables

Table 1	Equilibrium Equations in Electrolyte NRTL Model, Mole Fraction-Based
Table 2	Regressed Binary Interaction Parameters for the Electrolyte NRTL Model
Table 3	Reduced Equilibrium Reactions without Hydroxide and Hydronium Ions
Table 4	Equilibrium Constants in Electrolyte NRTL Model, Mole Fraction-Based
Table 5	Default Binary Interaction Parameters for the Electrolyte NRTL Model
Table 6	Regressed Values for Parameters in Equilibrium Constant Temperature Dependent Equation
Table 7	Piping Checklist
Table 8	Material & Energy Balance Case Specification
Table 9	Stream Flow Specification
Table 10	Equipment Specification
Table 11	Utility Specification
Table 12	New Equipment Status
Table 13	Equipment Specification List

Introduction

The objective of this work is to improve the process for CO₂ capture by alkanolamine absorption/stripping by developing an alternative solvent, aqueous K₂CO₃ promoted by piperazine. This work will expand on parallel bench scale work with system modeling and pilot plant measurements to demonstrate and quantify the solvent process concepts.

The bench-scale and modeling work is supervised by Gary Rochelle. Frank Seibert is supervising the pilot plant. Two students supported by the Texas Advanced Technology Program (Tim Cullinane and Marcus Hilliard) have made contributions this quarter to the scope of this project. Two graduate students (Babatunde Oyenekan and Eric Chen) have been supported by this DOE contract since January 2003 for direct effort on the scope of this contract. One student (Terraun Jones) has been supported by industrial funding.

Experimental

The following sections of this report detail experimental methods:

Subtask 2.1 (Pilot plant test plan) describes methods for piperazine analysis by gas chromatography.

Subtask 2.2 (Design, Modifications, Order Equipment and Packing Materials) updates progress in the design and modification of the pilot plant for future testing.

Results and Discussion

Progress has been made on four subtasks in this quarter:

Subtask 1.1 – Modify Vapor-Liquid Equilibrium (VLE) Model

Tim Cullinane has developed a new set of parameters to be used with the stand-alone electrolyte-NRTL model for CO₂/water/potassium carbonate/piperazine.

Marcus Hilliard has entered parameters for the (NRTL) model in AspenPlus.

Subtask 1.3 – Develop Integrated Absorber/Stripper Model

Babatunde Oyenekan has developed a mathematical framework to simulate a stripper with Aspen Custom Modeler.

Subtask 2.1 – Pilot Plant Test Plan

Terraun Jones has applied gas chromatography to measure the oxidative degradation of piperazine.

Subtask 2.2 - Design, Modifications, Order Equipment and Packing Materials

Eric Chen has updated the schedule for the pilot plant modification. The dricital path is the welding contract. The new heat exchangers have all been received in Austin.

Conclusions

1. The stand-alone NRTL electrolyte model with regressed parameters represents the following sets of data;
 - a. Piperazine activity coefficients in piperazine/H₂O (from UNIFAC).
 - b. Water activity in potassium carbonate/H₂O.
 - c. CO₂ vapor pressure over K₂CO₃/K₂HCO₃/H₂O.
 - d. CO₂ vapor pressure and NMR speciation in piperazine/CO₂/H₂O.
 - e. CO₂ vapor pressure and NMR speciation in piperazine/K₂CO₃/K₂HCO₃/H₂O
2. The physical solubility of CO₂ is a weak function of piperazine, but decreases as much as a factor of four in concentrated K⁺ solutions.
3. The oxidative degradation rate of piperazine is 2 to 5 mM/hr and may be limited by oxygen mass transfer.
4. The absorber stripper pilot plant is on schedule to start shakedown in November 2003.

Future Work

We expect the following accomplishments in the next quarter:

Subtask 1.1 – Modify Vapor-Liquid Equilibrium (VLE) Model

Trouble-shooting will clean up the electrolyte-NRTL model in Aspen Plus.

Subtask 1.3 – Develop Integrated Absorber/Stripper Model

A stripper model will be implemented in Aspen Custom Modeler.

Subtask 2.1 – Pilot Plant Test Plan

A detailed test plan will be developed for the first campaign.

Subtask 2.2 - Design, Modifications, Order Equipment and Packing Materials

Piping modifications will be completed.

Task 1 – Modeling Performance of Absorption/Stripping of CO₂ with Aqueous K₂CO₃ Promoted by Piperazine

Subtask 1.1a – Modify Vapor-Liquid Equilibrium (VLE) Model – Stand-alone FORTRAN Model

by J. Tim Cullinane

(Supported by the Texas Advanced Technology Program, Grant no. 003658-0534-2001)

Introduction

This report presents the continuing development of aqueous potassium carbonate-piperazine mixtures for CO₂ removal from flue gas. As of March 2003, data on CO₂ partial pressure, piperazine speciation, and CO₂ absorption rates had been collected (1). Also, a rigorous thermodynamic model was developed to predict equilibrium and speciation in potassium carbonate-piperazine mixtures.

The equilibrium model is still under development, but key changes have been made. First, τ parameters implied from UNIFAC predictions were revisited and applied over a broader range of temperatures. Also, the data set for K₂CO₃ was improved by including more points from various researchers. Several other changes were explored, but were not included due to the added complexity and the minimal performance improvements.

Concurrent with the modeling work, the physical solubility of CO₂ in the salt-amine mixtures was measured and will be used to improve the physical significance of future kinetic modeling.

Experimental (Equilibrium Modeling)

The thermodynamic model used is the electrolyte Non-Random Two-Liquid model (electrolyte NRTL) developed by Chen *et al.* (2) and commonly used for modeling acid gas systems. The model uses binary interaction parameters, τ , to represent the interaction of molecules and ions on excess Gibbs free energy. The binary interaction can be represented as

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$$

where i and j represent differing species.

The electrolyte NRTL uses three terms to represent excess Gibbs energies. The Pitzer-Debye-Huckel term is a long-range contribution describing ion-ion interactions at low concentrations. The Born correction accounts for changes in the dielectric constant of the solution as the solvent reference state changes. Short-range contributions, dominant at high concentrations, are represented by the NRTL model (3). The excess Gibbs energy of the three terms are added to give a total excess Gibbs energy.

$$\frac{g_{ex}^*}{RT} = \frac{g_{ex PDH}^*}{RT} + \frac{g_{ex Born}^*}{RT} + \frac{g_{ex NRTL}^*}{RT}$$

The excess free energy is related to the activity coefficient by

$$\ln \gamma_i = \frac{g_{ex}^*}{RT}$$

A more thorough discussion of electrolyte NRTL theory as it pertains to gas treating solvents can be found in Austgen (4) and Posey (5).

In the model used in this work, all molecule-molecule and ion pair-ion pair parameters are set to zero. All acid gas-ion pair and ion pair-acid gas parameters, and molecule-ion pair and ion pair-molecule parameters not regressed were fixed at values of 15 and -8 respectively. Non-regressed water-ion pair and ion pair-water parameters were fixed at values of 8 and -4 . Also, all τ 's are assumed to have no temperature dependence unless otherwise specified. Henry's constant of CO_2 is assumed to be that of CO_2 in water. All reactions considered and the associated equilibrium constants are presented in Table 1.

Table 1. Equilibrium Equations in Electrolyte NRTL Model, Mole Fraction-Based

Equilibrium Constant	$\ln K_i = A + B/T + C \ln T$			Source
	A	B	C	
$K_{HCO_3^-} = \frac{x_{HCO_3^-} \cdot x_{H_3O^+}}{x_{CO_2} \cdot x_{H_2O}^2}$	231.4	-12092	-36.78	(5, 6)
$K_{CO_3^{2-}} = \frac{x_{H_3O^+} \cdot x_{CO_3^{2-}}}{x_{HCO_3^-} \cdot x_{H_2O}}$	216.0	-12432	-35.48	(5, 6)
$K_w = \frac{x_{H_3O^+} \cdot x_{OH^-}}{x_{H_2O}^2}$	132.9	-13446	-22.48	(5, 6)
$K_{PZH^+} = \frac{x_{PZ} \cdot x_{H_3O^+}}{x_{PZH^+} \cdot x_{H_2O}}$	4.964	-9714	0.0	(7)
$K_{PZCOO^-} = \frac{x_{PZCOO^-} \cdot x_{H_3O^+}}{x_{PZ} \cdot x_{CO_2} \cdot x_{H_2O}}$	-47.05	11268	0.0	This Work
$K_{H^+PZCOO^-} = \frac{x_{PZCOO^-} \cdot x_{H_3O^+}}{x_{H^+PZCOO^-} \cdot x_{H_2O}}$	-22.65	-680	0.0	This Work
$K_{PZ(COO^-)_2} = \frac{x_{PZ(COO^-)_2} \cdot x_{H_3O^+}}{x_{PZCOO^-} \cdot x_{CO_2} \cdot x_{H_2O}}$	-14.96	380	0.0	This Work

Results and Discussion

The development of a thermodynamic model for potassium carbonate-piperazine requires the regression of τ for significant contributing species. τ 's were regressed sequentially for multiple, independent data sets. The following forms are used for molecule-molecule and for ion pair-molecule or molecule-ion pair parameters respectively.

$$\tau = A + \frac{B}{T(K)} \quad \text{and} \quad \tau = A + B \cdot \left(\frac{1}{T(K)} - \frac{1}{353.15} \right)$$

The regression sequence and the parameters are shown in Table 2. After each regression, parameter values were fixed before proceeding to the next step to maintain a more thermodynamically consistent model. Parameter regression was aided by the use of a non-linear regression program named GREG (8). User defined parameters are adjusted until the least squares difference of experimental and predicted values is minimized.

Table 2. Regressed Binary Interaction Parameters for the Electrolyte NRTL Model

Step	Interaction	A	σ_A	B	σ_B	τ , 298K
1	H ₂ O, PZ	1.67	0.42	Def.**	-	1.67
	PZ, H ₂ O	10.10	0.25	-3606.3	Indet.*	-2.00
2	H ₂ O, K ⁺ , CO ₃ ²⁻	9.27	0.18	1466.5	588.5	10.04
	K ⁺ , CO ₃ ²⁻ , H ₂ O	-4.49	0.04	-344.6	113.7	-4.67
3	H ₂ O, K ⁺ , HCO ₃ ⁻	7.61	0.04	3246.2	Indet.*	9.31
	K ⁺ , HCO ₃ ⁻ , H ₂ O	-3.37	Indet.*	-763.2	78.6	-3.77
4***	H ₂ O, PZH ⁺ , HCO ₃ ⁻	8.32	0.16	Def.**	-	8.32
	H ₂ O, PZH ⁺ , PZCOO ⁻	6.09	3.88	8840.1	5200.4	10.71
	PZH ⁺ , PZCOO ⁻ , H ₂ O	-5.31	0.81	Def.**	-	-5.31
	H ₂ O, PZH ⁺ , PZ(COO ⁻) ₂	5.01	0.43	Def.**	-	5.01
	PZ, PZH ⁺ , PZCOO ⁻	Def.**	-	-9210.2	13219.0	10.19
	PZH ⁺ , PZCOO ⁻ , PZ	-12.51	3.09	Def.**	-	-12.51
	CO ₂ , PZH ⁺ , HCO ₃ ⁻	7.17	1.26	Def.**	-	7.17
5***	H ₂ O, K ⁺ , PZCOO ⁻	10.59	0.74	-27297.3	6428.8	-3.67
	K ⁺ , PZCOO ⁻ , H ₂ O	-2.48	0.21	Def.**	-	-2.48
	H ₂ O, K ⁺ , PZ(COO ⁻) ₂	4.37	4.10	-25859.4	22296.0	-9.13

* Indeterminate: Represents a high correlation between parameters.

** Default parameters used.

*** In progress.

The first step defines the infinite dilution activity coefficient of piperazine in water. Predictions of the UNIFAC thermodynamic model (9) were assumed accurate for several compositions and temperatures ranging from 25 to 50°C. The parameters in the electrolyte NRTL model were adjusted to fit UNIFAC predictions.

In the second step, model parameters were adjusted to fit data for the activity of water in K_2CO_3 -water mixtures as reported in the literature. Boiling point elevation and vapor pressure data was readily available (10, 11, 12). Data modeled from electrochemical experiments were also found, but were excluded from the regression because useful data was the result of a model (13, 14, 15). A wide range of both temperature (289 to 393 K) and concentration (0.0 to 50 wt% K_2CO_3) were used in the model. The values of four regressed parameters are consistent with other salt solutions as reported by Chen *et al.* (2).

The third set of regressed parameters describes $KHCO_3$ behavior as interpreted from VLE data by Tosh *et al.* (16). A normalized parity plot of the predicted CO_2 partial pressures is shown in Figure 1. The figure shows a large degree of scatter among the data points. Within the spread, it appears that predictions of 20 wt% K_2CO_3 are centered lower than experimental values, predictions of 30 wt% K_2CO_3 agree with experimental data, and predictions of 40 wt% K_2CO_3 are centered higher than expected. This may be due to the experimental method used in the study. Or, a failure of the model to predict concentration effects on the temperature dependence may be to blame. Regardless, most points are predictable to within 20%.

Figure 1. Electrolyte NRTL Model Predictions of CO_2 Vapor Pressure in Aqueous Potassium Carbonate Solutions (Tosh *et al.*, 1959) Using Parameters Shown in Table 1

The fourth step utilized proton (^1H) NMR data for speciation of loaded piperazine solutions and total pressure data over similar solutions as reported by Kamps *et al.* (17) and Ermatchkov *et al.* (18). Additional vapor pressure data was found by Bishnoi (7).

The final regression in the sequence utilized past (1) and current ^1H NMR data on the speciation of loaded aqueous piperazine in the presence of potassium carbonate to obtain parameters describing potassium and piperazine interactions. Throughout the range of concentration and loading, the model demonstrates its versatility and accuracy of correctly predicting the speciation.

Using the model, speciation predictions were made in two solutions: 0.6 m PZ (Figure 2) and 3.6 m K^+ /0.6 m PZ (Figure 3). In the absence of potassium carbonate, piperazine is much more susceptible to protonation from the addition of CO_2 to the system. Model predictions show that protonated piperazine is the dominant species at $P_{\text{CO}_2^*} > 250$ Pa. This is significant due to the decreased amount of free amine available for reaction with CO_2 , potentially detracting from the rate of CO_2 absorption.

In contrast, the 3.6 m K^+ /0.6 m PZ solution contains much more of the carbamated species. Because piperazine carbamate is still reacts with CO_2 , this solution maintains a fast absorption rate. The carbonate successfully buffers the solution at a higher pH, preventing the protonation, and thus the loss, of reactive piperazine.

Future work with the model will require accurate predictions of VLE of various solutions. Parameters affecting the activity of CO_2 in solution will be regressed to fit partial pressure and total pressure data available for systems containing piperazine and potassium carbonate. These parameters will be coordinated with previously regressed parameters to redefine the speciation. Also, the model will be coupled with a rigorous rate code (7). Together the models will be used to regress kinetic parameters for modeling the absorption of CO_2 into K^+ /PZ mixtures.

Figure 2. Speciation in 0.6 m PZ at 333 K

Figure 3. Speciation in 3.6 m K⁺/0.6 m PZ at 333 K

Conclusions

The development of a physically significant kinetic model greatly depends on the accuracy to which liquid phase concentrations can be predicted. Current data allows sufficient modeling of piperazine, but gives no indication of the concentration of CO₂ in the aqueous phase. Experiments have been performed to allow a better estimation of this value.

The theory of gases suggests a proportional relationship between solubility and ionic strength of the solution. Other correlations have been developed based on the simple relation

$$\log \frac{H}{H^0} = KI$$

where H is the solubility in solution, H⁰ is the solubility in water, K is a proportionality constant, and I is the solution ionic strength.

Because CO₂ reacts with both CO₃²⁻/HCO₃⁻ and PZ, physical solubility cannot be directly measured. An analogy with the inert (in these systems) N₂O was used since it has a similar size and Lennard-Jones potential. Several investigators have used this analogy to derive CO₂ solubilities in salt and amine solutions (19, 20, 21). The solubility of CO₂ is calculated by

$$H_{CO_2} = H_{N_2O} \frac{H_{CO_2}^0}{H_{N_2O}^0}$$

The solubility of CO₂ was found for 0.0 to 1.8 m piperazine mixtures at 25 and 40°C and is presented in Figure 4. There is very little detectable change over the narrow concentration range of PZ, but there is a significant temperature dependence that is equivalent to that of water.

Figure 4. CO₂ Solubility in Aqueous PZ Solutions at 25 and 40°C

The solubility was also found for salt solutions and salt-amine mixtures (Figure 5). All ionic concentrations were represented by the nominal concentration of K₂CO₃ or KHCO₃. Experiments on K₂CO₃ and 70% KHCO₃/30% K₂CO₃ mixtures revealed solubilities closely matching those found in literature. The data show a difference in the effect of CO₃²⁻ and HCO₃⁻. Solubilities in PZ/K₂CO₃ mixtures closely match solutions that do not contain PZ, reflecting the mild influence of PZ in the concentrations examined. Values in PZ/KHCO₃ solutions differ significantly from those expected and may be attributable to the representation of the ionic concentration. This data will be incorporated into the thermodynamic model to aid in the future representation of kinetics.

Figure 5. CO₂ Solubility of K₂CO₃, KHCO₃, and PZ Mixtures at 25°C

Subtask 1.1b – Modify Vapor-Liquid Equilibrium (VLE) Model – Aspen Plus

by Marcus Hilliard
(Supported by this contract)

Introduction

The work presented in this subtask is the continuing development of a rigorous electrolyte non-random two-liquid (NRTL) thermodynamic model of potassium carbonate/piperazine (K_2CO_3/PZ) solvent for use in an Aspen Plus™ model of the absorption/stripping process. The model, which should predict the speciation and vapor pressure of carbon dioxide solvent composition and temperature, will be implemented in Aspen Plus™ to facilitate use of previous models in the integrated simulation.

Previously, development of the basic property data for piperazine species (PZH^+ , $PZCOO^-$, H^+PZCOO^- , $PZ(COO^-)_2$) that were not available in the Aspen Plus™ database was collected. Initial vapor-liquid equilibrium (VLE) results using a simplified equilibrium separations model (Flash II Column) in Aspen Plus™ for initial comparison to other successful K_2CO_3/PZ electrolyte NRTL models were obtained.

Experimental (Equilibrium Methods)

For this work, we have chosen to use the rigorous Electrolyte-NRTL activity coefficient method (ELECNRTL). According to Aspen Technology (22), “ELECNRTL model can represent aqueous and aqueous/organic electrolyte systems over the entire range of electrolyte concentrations with a single set of binary interaction parameters”. This model proposes five equilibrium reactions as an alternative to seven equilibrium reactions as suggested by Cullinane (1). Cullinane expanded a simple equilibrium model for monoethanolamine with piperazine (23) to include the impact of potassium ion associated with the potassium carbonate/piperazine system.

The system of equations was reduced by taking linear combinations to exclude the negligible hydroxide and hydronium ion molal concentrations of less than 10^{-4} and 10^{-8} , respectively. The equilibrium reactions are shown in Table 3.

Table 3. Reduced Equilibrium Reactions without Hydroxide and Hydronium Ions

The equilibrium constants also developed by Cullinane (24) were also adjusted to account for the new equilibrium reactions. The equilibrium constants are shown in Table 4.

Table 4. Equilibrium Constants in Electrolyte NRTL Model, Mole Fraction-Based

$\ln K_i = A + B / T$		
Equation #	A	B
1	-6.4967	-795.31
2	-26.119	10462
3	32.392	-9724.5
4	4.7783	-690.59
5	-2.5935	184.97

Cullinane proposed two-parameter equilibrium constant for the speciation of piperazine reactions involving the protonation of PZ and PZCOO⁻ and the reaction of CO₂ with PZ and PZCOO⁻. With the accuracy of a two parameter equilibrium model describing the main speciation, we felt that a two parameter equilibrium constant that described reactions involving the CO₂/HCO₃/CO₃⁻² buffer and the dissociation of water would introduce a negligible amount of error to our simulation. The three parameter equilibrium constants were linearly regressed by using the "least squares" method to determine a two parameter model.

Cullinane [24] also offered binary interaction parameters (τ) for the electrolyte NRTL model by sequentially regressing multiple, independent data sets (i.e. infinite dilution activity coefficients data, freezing point depression data, boiling point depression data, NMR data, etc.) using a generic, nonlinear regression package called Generalized REGression software (GREG) and compared to literature data. The predicted binary interaction parameters described piperazine speciation data within an absolute error of $\pm 5\%$ and incorporated it into the Aspen PlusTM model via Electrolyte GMELCC parameters.

Electrolyte NRTL pair parameters (GMELCC) in Aspen PlusTM employs a three parameter model. The GMELCC parameters used to model molecule - ion pair and ion pair – ion pair interactions. Electrolyte – electrolyte parameters are required only for mixed electrolytes with a common ion. Electrolyte – electrolyte parameters are generally negligible and can be assumed to be zero. However, electrolyte – electrolyte parameters can affect trace ionic activity coefficients significantly and can be important when dealing with salt precipitation. The default values are given in Table 5.

Table 5. Default Binary Interaction Parameters for the Electrolyte NRTL Model

<u>Interactions</u>	<u>Value</u>
Solute – ion pair	15.0
Ion pair – solute	-8.0
Water – ion pair	8.045
Ion pair – water	-4.072
Solute – salt	0.1
Water – salt	0.2

Vapor-liquid Equilibrium Benchmarks

The initial VLE bubble point comparison consisted of two cases:

- At a constant CO₂ loading of 1 m and potassium ion and piperazine concentrations of 5.0 m K⁺/2.5 m PZ and varying the Flash II column temperature from 25 – 80°C
- At constant temperature and pressure of 60°C and 0.17676 bar, respectively and varying the CO₂ loading molal concentrations from 0.5 – 2.5 m.

The potassium ion and piperazine concentrations were also held constant at 5.0 m K⁺/2.5 m PZ.

Results and Discussion

Vapor-liquid Equilibrium Benchmarks

For this initial benchmark, we wanted to see if our model would produce the same trends that other researchers have commented on specifically, increasing temperature at a constant loading and increasing the CO₂ loading at a constant temperature. As the temperature increases the concentration of free piperazine should increase and conversely the concentration of bicarbonate species (HCO₃⁻) decreases. On the other hand, as the CO₂ loading is increased the concentration of bicarbonate increases and the concentration of free piperazine decreases.

For the initial case with a constant CO₂ loading of 1 m and potassium ion and piperazine concentrations of 5.0 m K⁺/2.5 m PZ and varying the Flash II column temperature from 25 – 80°C the concentration of free piperazine did increase, but the concentration of bicarbonate did not decrease as shown in Figures 6 and 7.

Figure 6. VLE of PZ Species in Aqueous K⁺/PZ at constant loading of 1 m of CO₂

Figure 7. VLE Species in Aqueous K⁺/PZ at constant loading of 1 m of CO₂

The departure of the bicarbonate species from the observable trend suggests that the model does not accurately accounting for the temperature effects of the system. Several reasons could explain this departure:

1. The interaction parameters regressed by Cullinane are different in this system and need to be regressed in Aspen Plus.
2. The reference state in Aspen is affecting the temperature dependence of the bicarbonate species as compared to the reference state that Cullinane defined.

For the second case with a constant temperature of 60°C and potassium ion and piperazine concentrations of 5.0 m K^+ /2.5 m PZ and varying the Flash II column CO_2 loading from 0.5 – 2.75 m the concentration of free piperazine did decrease, and the concentration of bicarbonate did increase as shown in Figures 8 and 9. But the initial increase in $PZ(COO^-)_2$ mole fraction seen in Figure 8 is uncommon.

Figure 8. VLE of PZ Species in Aqueous K^+/PZ at 60°C

Figure 9. VLE Species in Aqueous K⁺/PZ at 60°C

Conclusions

Observable trends in the potassium carbonate/piperazine vapor-liquid equilibrium system showed promise for describing the piperazine speciation at different loadings of carbon dioxide but the temperature dependence of the model further warrants study.

Future Work

One recommendation for future work is to expand the model to accurately predict various VLE data sets. Binary interaction parameters will be regressed using the Aspen Plus built-in regression package and to sequentially regress multiple, independent data sets as performed by Cullinane. Then the model will be combined with a rigorous rate code developed by Bishnoi (23) for kinetic parameter regression analysis to model the absorption of CO₂ in potassium carbonate/piperazine systems.

Subtask 1.3 – Develop Integrated Absorber/Stripper Model – ACM Model for Stripper

by Babatunde Oyekan
(Supported by this contract)

Introduction

We are developing a stripper submodel in Aspen Custom Modeler (ACM) for an overall model of CO₂ absorption/stripping by an aqueous solution of potassium carbonate and piperazine. This quarter, the equations to be included in the model have been formulated. Correlations based on flash calculations are being developed to aid computation.

The Process

The rich solvent enters the stripper at a temperature of about 105°C. This is countercurrently contacted with steam, which is generated in the reboiler and condenses as it rises through the column. The lean solvent leaves the bottom at 120°C. The high temperatures give reactions in the fast to instantaneous reaction regime.

Stripper Modelling

The stripper will be represented by a rate-based model in Aspen Custom Modeler rather than by an equilibrium model. At the high temperature of the stripper, the equilibrium partial pressure of the CO₂ is appreciable and the reactions are reversible. Desorption of CO₂ can occur due to (a) flashing at the stripper feed (b) normal mass transfer in the stripper and (c) boiling in the reboiler.

Experimental

Aspen Custom Modeler

The stripper is being modelled in the Aspen Custom Modeler simulation environment (25). Aspen Custom Modeler represents processes with high-level equations. Equation solvers are built in so it does not require solution methods as in other high level languages such as FORTRAN and C. It has the capacity of reducing computation time and has a low risk of failure when compared to other programming languages. ACM can also be incorporated as a block in AspenPlus.

Why use ACM?

The reactions that occur in the stripper fall between the fast and instantaneous reaction regimes. Fast reactions are those in which the specific rate of mass transfer is a unique function of the physicochemical properties of the system and independent of the hydrodynamic factors. Typical Hatta numbers for such reactions are greater than two. Instantaneous reactions are reactions with very high rate constants and are therefore very fast. AspenPlus (RateFrac) has difficulty modeling reactions in the fast and instantaneous regimes. ACM has that capability and is preferred for modelling the stripper.

A base case is being developed with aqueous MEA before switching to a mixture of K_2CO_3 and piperazine. Upon modelling and validating the MEA results, the model will be expanded to simulate the pilot plant operation using an aqueous solution of K_2CO_3 /Piperazine system. The performance of such a system will also be predicted.

Simulations have been run and some correlations are being put together to reduce the need for the use of external add-ons like C or FORTRAN subroutines that are looped sequentially. The use of Aspen Properties Plus to call the physical properties of the components for use on ACM is an added advantage. ACM affords the user the ability to change existing formulation without having to re-write codes. User-defined equations can be used from scratch. The combination of modelling with experimentation will yield more efficient systems.

Model Formulation

Column Specifications

The following specifications are required.

- The height of packing
- The diameter of the tower
- The nominal diameter of the packing
- The reboiler duty

The operating variables are:

- The flow rates of all the species
- The steam rate
- The rich loading
- The operating temperature of the stripper

The physical properties required are the heat of reaction and the heat of vaporisation

Method of Solution

Initial guesses of the rich loading and temperature profile will have to be made. The interfacial partial pressure of CO_2 will be calculated via Henry's law and chemical equilibrium will establish the liquid phase compositions (speciation).

Accurate equilibrium expressions are difficult to obtain because the liquid phase becomes highly non-ideal as CO_2 is being absorbed. The ionic strength indicates the degree of non-ideality.

The equations to be solved in this model are

1. Equilibrium relationships
2. Total Amine concentration
3. Total CO_2 concentration
4. Total Water concentration

When these equations are solved, the bulk liquid concentrations can be determined. The interfacial concentrations are determined by mass transfer relationships.

The mass transfer parameters required are the gas phase mass transfer coefficient, k_g , liquid phase mass transfer coefficient, k_g' and the interfacial area per unit volume, a . These parameters depend on the contacting device to be modelled. The desorption process is enhanced as a result of the chemical reaction occurring. The limiting cases are those of very slow reaction and instantaneous reaction. In the very slow reaction regime the chemical reaction has no effect on the rate. Diffusion is the dominant factor in this region. In the instantaneous regime, the rate constant, k , is a large finite value. The reaction is considered to be in equilibrium at all points in the liquid. At the lean end of the stripper, solution loading is low and the protonated amine concentration is low and the free amine concentration is high. The overall effect is a low equilibrium partial pressure.

The other regimes are the slow reaction regime and the fast reaction regime. In the fast reaction regime, diffusion and reaction take place simultaneously i.e. they are parallel steps. The reactant reacts completely in the film. In this regime, the specific rate of mass transfer is a unique function of the physicochemical properties of the system and is also dependent on the hydrodynamic factors.

Equations for Reactions in the Stripper

The equilibrium reactions that occur in the stripper determine speciation. These equations are:

The above equations have ten variables in six equations. Four equations are needed to solve this problem.

(a) The CO_2 balance

$$X_{\text{CO}_2,\text{T}} = X_{\text{CO}_2} + X_{\text{HCO}_3^-} + X_{\text{CO}_3^{2-}} + X_{\text{MEACOO}^-} \quad (6)$$

(b) The MEA balance

$$X_{\text{MEA},\text{T}} = X_{\text{MEA}} + X_{\text{MEA}^+\text{H}} + X_{\text{MEACOO}^-} \quad (7)$$

(c) The total mole fraction balance

$$1 = x_{CO_2} + x_{H_2O} + x_{MEA} + x_{MEA^{H+}} + x_{H_3O^+} + x_{HCO_3^-} + x_{CO_3^{2-}} + x_{OH^-} + x_{MEACOO^-} \quad (8)$$

(d) The charge balance

$$0 = 2x_{CO_3^{2-}} + x_{HCO_3^-} + x_{OH^-} + x_{MEACOO^-} - x_{H_3O^+} - x_{MEA^{H+}} \quad (9)$$

Stripping occurs as long as $P^* > P$

$$P^* = Hx \quad (10)$$

where P^* = partial pressure of CO₂ in equilibrium with the liquid.

H = Henry's law constant

x = concentration of CO₂ in the liquid phase.

Dang (26) expressed the Henry's law constant as

$$H_{CO_2,MEA} \text{ (atm/mole.L)} = R \exp(-2625/T(K)) + 12.2 \quad (11a)$$

where

$$R = (\exp(A/T(K) + B)x_1 + hI) \quad (11b)$$

x_1 = mole fraction of amine in the unloaded solution

H = Van Krevelen constant

I = ionic strength

$A = 5076$

$B = -16.699$

Dang ignored the hI term.

Input Parameters

Correlations for calculating local mass transfer coefficients based on Onda et al. (27) and Wilson (28) will be used to calculate the mass transfer coefficients and effective area of contact.

The material balance equations needed are:

For the liquid phase

$$\frac{\partial}{\partial t} U_{ij} = -\frac{\partial}{\partial z} (L_{ij} x_{ij}) + (n_{ij} da + R_{ij} \phi_{ij}) A_c \quad i = 1, \dots, n \quad (12)$$

where

U = liquid holdup in moles

L_j = liquid flowrate on segment j

n_{ij} = molar flux of component i on segment j
 a = specific gas-liquid interfacial area
 R_{ij} = reaction rate of component i on segment j
 ϕ = volumetric holdup
 A_c = cross sectional area of tower

For the vapor phase

$$0 = \frac{\partial}{\partial Z}(G_{ij}y_{ij}) - (n_{ij}da - R_{ij}\phi_{gas})A_c \quad i=1, \dots, m \quad (13)$$

The above equations are subject to the constraints

$$\begin{aligned} \sum x_i &= 1 \\ \sum y_i &= 1 \end{aligned} \quad (14)$$

The total holdup U_t is related to the holdup on a segment U_{ij} by the expression

$$U_{ij} = x_{ij}U_t \quad (15)$$

The total holdup U_t is given by

$$U_t = \rho_l * \text{vol frac} * A_c * dz \quad (16)$$

ρ_L = density of the liquid

vol frac is the volume fraction of free space in column.

The flux of CO_2 (based on the liquid phase) is defined as

$$\text{Flux} = k_g'(P_{\text{CO}_2,i} - P_{\text{CO}_2*}) \quad (17)$$

where

$P_{\text{CO}_2,i}$ = partial pressure of CO_2 at the interface

P_{CO_2*} = equilibrium partial pressure of CO_2

In general, the liquid phase mass transfer coefficient is a function of temperature and loading.

The energy balance equations are:

For the liquid phase

$$\frac{\partial U_{l,j}}{\partial t} * H_{l,j} = - \frac{\partial (L_{l,j})}{\partial Z} * H_{l,j} + N_{H,j} + Q_l \quad (18)$$

where

$H_{l,j}$ = enthalpy of the liquid phase on segment j

NH_j = heat flux on segment j

Q_l = heat added or withdrawn from liquid phase on segment j

For the vapor phase

$$0 = -\frac{\partial(V_{ij})}{\partial z} * H_{v,j} + NH_j + Q_v \quad (19)$$

where

$H_{v,j}$ = enthalpy of the vapor phase on segment j

NH_j = heat flux on segment j

Q_v = heat added or withdrawn from vapor phase on segment j

To ease the computations, correlations are being developed that express the equilibrium partial pressure of CO_2 as a function of loading and temperature. The temperature effects are also seen in determining the equilibrium constant.

Adding equations (4) and (5) we have

The equilibrium constant is given by

$$K = \frac{[MEA]^2 P_{CO_2}}{[MEAH^+][MEACOO^-]} \quad (21)$$

The equilibrium partial pressure of CO_2 is then

$$P_{CO_2} = \frac{K[MEAH^+][MEACOO^-]}{[MEA]^2} \quad (22)$$

From the total MEA concentration

$$MEA_T = MEAH^+ + MEA + MEACOO^-$$

we know that

$$MEAH^+ = \lg * MEA_T$$

$$MEACOO^- = \lg * MEA_T$$

The total CO_2 concentration is

$$CO_{2T} = MEACOO^- + HCO_3^-$$

Substituting for the MEA, MEA^+ and MEACOO^- in the expression for the equilibrium constant gives

$$P_{\text{CO}_2} = K \frac{\text{ldg}^2}{(1 - 2\text{ldg})^2} \quad (23)$$

where ldg = gas loading = moles of CO_2 per mole of amine.

The equilibrium constant K is generally a function of temperature, gas loading and amine concentration.

The equilibrium constant, temperature and heat of desorption are related by the expression

$$\frac{d \ln K_{\text{des}}}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H_{\text{des}}}{R} \quad (24)$$

where

K_{des} = desorption equilibrium constant

H_{des} = heat of desorption

T = temperature in Kelvin

R = gas constant

The heat in the stripper Q_{stripper} in J/mol

$$Q_{\text{stripper}} = \frac{\Delta H_{\text{des}}}{\text{mol CO}_2} + \frac{\Delta H_{\text{H}_2\text{O}} n_{\text{H}_2\text{O}}}{\text{mol CO}_2} + M_{\text{steam}} C_{p_{\text{steam}}} \Delta T \quad (25)$$

M_{steam} = mass of steam

The terms on the right hand side of the expression above are the heat of desorption of per mole of CO_2 , the heat of vaporisation of water per mole of CO_2 and the sensible heat due to the difference in temperature of the rich loading and the operating temperature of the stripper.

Results and Discussion–Work In Progress

At present, the partial pressure as a function of loading and temperature is being correlated so that the ACM model can be run without need for an external add-on that requires a sequential solver. The correlations for P_{CO_2} and K (equilibrium constant) will be inputted in ACM and the equations can be solved without a need for a well-defined sequence. Finishing touches are being put to the preliminary model and preliminary results will be presented in the next report.

The equilibrium constant is temperature dependent. The equation that defines this is given by

$$\ln K = A + \frac{B}{T} + C \ln T + DT \quad (26)$$

The parameters obtained for Freguia (29) are given in Table 6.

Table 6: Regressed Values for Parameters in Equilibrium Constant Temperature Dependent Equation

Rxn #	A	B	C	D
1	132.89	-13445.9	-22.48	0
2	231.46	-12092.1	-36.78	0
3	216.05	-12431.7	-35.48	0
4	-3.03	-7008.36	0	-0.003135
5	-0.52	-2545.53	0	0

Conclusions–Proposed Work for the Next Quarter

- Complete the correlations and present preliminary results of the stripper modelling for the base case i.e. stripping of CO₂ using MEA.
- Attempt at developing a correlation for the equilibrium constant as a function of temperature and loading
- Refine the model.
- Initiate modelling the absorber and stripper for the K₂CO₃/PZ system.
- Sensitivity analysis will be performed on process variables to determine operating conditions that will require low steam requirement.

Task 2 – Pilot Plant Testing

Subtask 2.1 – Pilot Plant Test Plan – Development of Analytical Methods

by Terraun Jones
(Supported by other industrial sponsors)

Introduction

Monoethanolamine (MEA) and piperazine are amines that have been proposed for use in aqueous scrubbing for CO₂ capture from flue gas. Liquid analysis techniques are required to determine operating concentrations of these amines and their degradation products. This report will show revised gas chromatography methods devised for alkanolamines, piperazine, and possible amine products that result from oxidative degradation of the solutes and quantify entrainment and evaporation for piperazine degradation in promoted potassium carbonate solutions.

Experimental

Gas Chromatography

Method Setup

The Gas Chromatograph was an HP 5890 with an HP 7673 Autoinjector. The column was an HP-5 capillary column with a .53mm and 1.5μm lining. Two column lengths were used, 30 feet and 10 feet. The system was a split/splitless injector with helium as the carrier gas. The ratio of column gas rate to overall gas rate was 20 with column gas rate of 10 ml/min. All of this was checked with a bubble flowmeter. The rest of the gas was vented. The split was designed to lessen the work load on the column for separations by diluting the vaporized solution. Air, hydrogen, and a makeup gas of helium were used for the FID detector for better peak detection. The air rate is 400 ml/min. The hydrogen rate is 30 ml/min and the Makeup Gas rate is 10 ml/min.

The temperature ramping system was optimized to achieve separation of components that come out close together and still keep the sharpness of the peaks. Two programs, one for the short (10 feet) column and one for the long (30 feet) column were used. The run time for the long column was 13 minutes. The first five minutes run isothermally at 60°C. The temperature was then ramped up to 180°C at 15°C/min. The short column started at 40°C for one minute, and then is ramped to 120°C at 20°C/min. The injector and detector were set at 220°C so we do not achieve thermal degradation of the components. The system was computer automated with Galaxie Chromatogram software, which fully controls the injection and detection process.

Results

The long temperature ramp was used to detect small acids such as formate and acetate and for compounds that are similar to the probable degradation products for piperazine. Figure 10 shows a sample solution of piperazine, Hydroxyethyl-ethylenediamine (HEEDA) and Imidazolidinone (IMI, also known as ethylene urea),

formic acid, and acetic acid and water with roughly equal mass analyzed by GC. The first peak at 0.7 minutes is ethanol, which is used for internal standard calibration. Formate and acetate came out at roughly the same time, 1.2 minutes. Piperazine elutes at roughly 4 minutes. HEEDA elutes at 9.6 minutes and IMI came out at 11.0. The ramping sharpens up the piperazine (MW 86.13 grams/mole) peak. Water is not detected in the FID and therefore has no peak.

Figure 10. Gas Chromatogram for Long Column Amine Calibration

The method for the short column is designed for quick analysis. Since previous analysis of degradation solutions show very little peak detection around the piperazine peak, there is no necessity for a detailed analysis in these regions. Figure 11 shows a GC readout for piperazine, ethanol, IMI, HEEDA, and water at roughly equal weights. Ethanol comes out at 0.3 minutes, piperazine comes out at roughly 0.9 minutes, HEEDA comes out at 2.5 minutes and IMI comes out at 3.5 minutes. Formate and acetate was also used but the results were inconclusive. The peaks are sharper because of the shorter column, which lower the likeliness of extended bonding to the capillary walls. Temperatures do not have to be as high for shorter columns, so thermally unstable compounds are better analyzed under these conditions. However, if there are compounds that are similar and elute closely, the short column will not give a sufficient separation necessary for analysis. This method was used primarily for piperazine analysis only.

Figure 11. Gas Chromatogram for Short Column Amine Calibration

Piperazine Degradation

Experimental Setup

Air at 1L/min was mixed with CO₂ gas at 20 cc/min to make a 2% CO₂ stream for experiments with rich solution, or just plain air for experiments with lean solution. This stream was saturated at reactor temperature in a 3L water bath. The saturated air stream was sent to the reactor. The reactor is glass, jacketed, and connected to a temperature bath to regulate the temperature. A mist eliminator was added to control entrainment in the system, which will be discussed later. Syringe samples were taken once a day at approximately 24 hours intervals over 7 days. The solutions were analyzed by GC or IC for content. The volume and mass of the sample was recorded as well as the time and the volume in the reactor. The volume of the reactor was recorded by measuring the height of the solution. These measurements accounted for water balances and help calculate the overall mass of components in the system

Results and Discussion

Overall Piperazine Loss

Using GC, degraded piperazine solutions were analyzed. These solutions contain potassium bicarbonate at high concentration and iron at low concentration. These solutions are diluted by two orders of magnitude on a mass basis with water to prevent clogging due salt collection. After the weight percents are found, the concentration was calculated. The concentrations in the figures are not the actual concentrations in the reactor, but the molar mass of the species divided by the original volume of solution in the reactor. This is done because it is assumed that volume changes in the reactor are due to water either being evaporated or put in. Equation 27 is used for calculating concentration.

$$\text{Conc} \left(\frac{\text{mol}}{\text{L initial solution}} \right) = \frac{\text{wt}\%_{\text{analyte}} \rho_{\text{sample}} V_{\text{rxter}}}{\text{MW}_{\text{amine}} V_{\text{initial}}} \quad (27)$$

It is assumed that since the samples are diluted and rapidly heated, all carbamates are returned to the original amines. Of great importance is the same peaks that appear in the peroxide experiment appear in the reaction chromatogram.

Figure 12. Piperazine Loss for 5.0/2.5 Solutions

Piperazine is plotted for four experiments. The experiments are 5.0 Molal KHCO_3 /2.5 Molal Piperazine in lean and rich solutions at 40 and 60°C. The rate of Piperazine loss for 40°C and rich is 2.7 mM/hr, 60°C and rich is 7.7 mM/hr, 60°C and lean is 4.2 mM/hr, and 40°C and lean is 5.4 mM/hr over the course of each experiment. The 60°C and rich experiment did not last as long as the others, so it did not have the same opportunity to reach a pseudo steady state. These loss rates are roughly double to triple the loss rates that were discussed in the previous paper. Since the concentrations are double the concentration of previous experiments, there is roughly a first order increase in the rates. The experiments could also be only as good as the dissolution of oxygen into solution, which is a mass transfer controlled process.

Evaporation and Entrainment

If the rate of piperazine disappearance will be used to characterize degradation, it is important to quantify all the ways piperazine can leave the reactor system. Since a continuous flow rate of gas is bubbling into the reactor and leaving the system for an extended period of time, evaporation and entrainment can become significant. Preliminary evaporation data shows as high as a 10 ppm concentration of piperazine in

the gas phase over highly concentrated piperazine solutions with no salt present. Adding potassium salt will lower the concentration in the gas phase. Using 10 ppm as a ceiling for evaporation, the evaporation rate was calculated to be .077 mM/hr, or roughly 4% of the overall piperazine loss. As the piperazine concentration decreases and the potassium increases, this number can go down as much as 80%, making it insignificant in the overall loss in the system.

Entrainment appears to be a much more significant source of piperazine loss than evaporation. Figure 13 shows a quantified chart of entrainment each day. The calculation is done based on density correlations. Density is a strong function of potassium ion concentration, but a weak function of piperazine concentration (1). Concentrations were calculated using density if there is only dilution due to water. If this concentration is greater than the concentration calculated from the experimental density, the change is due to entrainment. Based on this, the calculated entrainment rate for 40°C and rich is 0.2 mM/hr, 60°C and rich is 5.9 mM/hr, 60°C and lean is 1.8 mM/hr, and 40°C and lean is 0.2 mM/hr. The mist eliminator did a decent job of decreasing the entrainment for a couple of the experiments.

Figure 13. Entrainment Calculated for 5.0/2.5 Experiments

Conclusions

The GC temperature ramping system was changed from previous experiments to sharpen the piperazine peaks for better precision and accuracy. It is also for compounds that elute at late times. Entrainment is roughly 10% of the overall loss of piperazine, significantly less than past experiments and evaporation is relatively insignificant in the system. The resulting degradation rate for 40°C and rich is 2.5 mM/hr, 60°C and rich is 1.9 mM/hr, 60°C and lean is 2.4 mM/hr, and 40°C and lean is 5.2 mM/hr over the course of the experiment. The resulting degradation rates still show a loss of piperazine being roughly the same as other commonly used alkanolamines for acid gas scrubbing, and are

roughly twice that of the previously done experiments. To better measure entrainment, ion chromatography to measure potassium ion concentration or any other method is better suited.

Future Work

Piperazine degradation will be studied further. The extra components from the degradation will be identified through NMR. Different metals, such as vanadium and copper, will be used in the degradation reactions. Mass transfer analysis will be done on the reactor system to determine whether the system is mass transfer limited. The analysis methods utilized for degradation will also be extended to upcoming pilot plant research on these solutions.

Subtask 2.2 – Design, Modifications, Order Equipment and Packing Materials

by Eric Chen
(Supported by this contract)

Project Management

In this quarter, the bi-monthly meetings were continued to ensure that tasks were completed according to the project schedule (Figure 14). From the Gantt chart, the critical path for the project was determined to be the welding contract and subsequent construction of multiple skid assemblies. The welding bid contract was submitted a few weeks behind schedule due to complications related to university administration. Deadline for the welding bids is July 17. The University Physical Plant has initiated construction of the skids. The tentative start-up date for the pilot plant is still slated for the beginning of November. Commencement of Campaign 1 will be contingent on the initial operational difficulties encountered during the troubleshooting phase of the pilot plant start-up.

Experimental

Piping Iso's/Welding Bid

The piping iso's for the plant piping modifications were completed. The drawings were first completed by hand and then inputted into Autocad 14. A total of 18 drawings were completed. Progress for the welding contract will be monitored using Table 7. Each drawing contains one or more piping lines. After each section of piping is fabricated, UT-SRP plant personnel will do an initial visual inspection. If the work is satisfactory, the section of pipe will undergo a hydro test to determine if there are any leaks. Final approval of the piping job will be contingent on completion of the three tasks. The welding contract was submitted to our purchasing department early June. However, a number of minor changes to the welding bid terms were made before UT Purchasing deemed it acceptable. Hence, the revised welding package did not go out for bid until late June. The bids will be opened on July 17th by UT-SRP and the selection of the welding contractor will be made within a week. Therefore, we anticipate the welding process for the major piping revisions to begin late July or early August.

Heat Exchangers/Support Racks

The three support racks for the heat exchangers and process instrumentation are in the process of being constructed. Piping and structural steel were purchased and delivered to the UT Physical Plant Welding Shop for fabrication. The support racks will need to be completed before the installation of the solvent heaters and cooler. The solvent cooler (H-107) from ITT Standard was delivered at the end of June. The design of the heat exchanger rack supports and skids were revised and are currently under construction. One of the three skids has been completed. Once the heat exchanger supports have been completed, the solvent cooler and the two heat exchangers (solvent heater) donated by Huntsman can also be mounted on the skid and installed within the

battery limits of the pilot plant. New gaskets, flanges, and stub ends were ordered for the two solvent heaters from Brown Fintube.

Figure 14. Gantt Chart for CO₂ Removal Project

Table 7. Piping Checklist

Drawing No.	Line	Fabrication (%)				Initial/Visual Inspection	Hydro Test	Final Approval
		25	50	75	100			
6100-601	P2001							
	P2004							
6100-602	P2003							
6100-603	P2005							
	P2021							
	P2022							
	P2023							
	P2027							
	P3003							
6100-604	P2010							
	P4013							
	P4014							
6100-605	P2013							
6100-606	P2014							
6100-607	P4014							
	P3002							
	P4013							
6100-609	LS2001							
	LC2002							
	CW2001							
	CW2002							
6100-610	P3001							
	P3015							
6100-611	P2003							
6100-612	P3006							
	P3007							
	P3008							
6100-615	P4001							
6100-616	P4002							
	P4007							
6100-617	P4002							
	P4017							
6100-621	P4016							
6100-622	P4017							
6100-630	AA4001							
6100-631	AA4004							

Air Cooler

The air cooler has been designed and ordered and will be shipped from Arizona on July 3rd. The original air cooler drawing was revised a number of times before being approved. The hanging brackets were modified to run the entire length of on each side. Two ¾-inch drain plugs were added to the drawing, one on the end of the panel covering the return bends and the other on the bottom pan of the coil. In addition, two ½-inch couplings were added to the transition ducts for the insertion of thermocouples. Two 10-inch cleanout access panels were also added to the manifold side of the transition ducts. The air cooler will need to be installed first before the welding process begins and before the other major pieces of equipment can be installed.

Process Instrumentation

A total of five Micro Motion[®] coriolis flowmeters were purchased at an academic discount from Emerson Process. The flowmeters were ordered and have been procured. Only one flowmeter was purchased with funds from this grant. Once the rack supports are completed, the flowmeters can be mounted. A temperature profile will be generated for the absorber column to characterize the temperature bulge. Temperature measurements in the absorber will be conducted using either thermocouples or RTD's and a thermal imaging camera. The inlet and outlet temperatures to the absorber of the gas and liquid will be measured using thermocouples. In addition, the core and skin temperatures TE-1 and TE-11 will be measured with thermocouples/RTD's (Figure 15). The objective is to determine the position and value of the maximum temperature. Since, the maximum temperature could conceivably be located in between two penetration points in the column, there is no way of directly measuring the core column temperature. Therefore, a thermal imaging camera will be used to measure surface temperatures and core temperatures will be taken at the two points adjacent and closest to the maximum temperature. The core temperature at the maximum may then be inferred from the two core and surface measurements.

Figure 15. Absorber Penetration Locations (TE). Note: Packing supports H10, H11, H12, H4, H5, H6.

Analytical

The setup for the analytical system is still in the design phase. Two CO₂ gas analyzers have been procured from Vaisala. It has been determined that the UT-SRP CO₂ analyzer cannot be used for this project. The analyzer would need to be sent back to the manufacture and hardware components would need to be replaced, thereby disabling the facility's ability to measure CO₂ at low concentrations.

In order to control and monitor the operating process, the CO₂ concentration in the liquid solvent will need to be determined. The CO₂ concentration in the liquid samples will be determined using a batch wet chemical method. The liquid samples are withdrawn and immediately diluted into cold water that has been purged with nitrogen gas. The dilution water will be chilled in an ice bath prior to the addition of the liquid sample and will be maintained in the ice bath up to the point of analysis. The sample will be further diluted 1000 times prior to laboratory analysis. The diluted sample will be injected directly into the total carbon analyzer. Output from the analyzer will be logged using a data acquisition card and recorded on a computer. The peaks will be integrated to obtain the CO₂ concentration in the liquid sample.

We are proposing to develop a continuous liquid CO₂ analyzer and are in the process of designing it. In a proposed design, liquid sample is withdrawn at a constant rate of 1 ml/min by a metering pump. The sample is pumped through a series of HCl acid impingers. The acid liberates CO₂ gas and nitrogen carrier gas transports the sample to a water knock out before being sent to the CO₂ gas analyzer.

Raw Materials: CO₂ Inventory

The design of the CO₂ system has been completed. The liquid solution will be made up from a mixture potassium carbonate (K₂CO₃) and bicarbonate (K₂HCO₃), with the addition of piperazine. A 47% liquid solution of potassium carbonate and technical grade potassium bicarbonate will be used. 68% piperazine solution will be donated by DOW Chemical. Based on a solution composition of 2.5 m piperazine and 2.5 m potassium carbonate, 1325 lb of piperazine, 1606 lb of K₂CO₃, and 520 lb of K₂HCO₃ are needed. The total cost of maintain the chemical inventory for one campaign is approximately \$4,600. The breakdowns of the costs are as follows: \$3,300 for piperazine, \$851 for potassium carbonate, and \$432 for potassium bicarbonate.

Packing Selection

An economic analysis for the absorber packing selection was commenced. Preliminary results showed that the majority of the annualized cost would come from the electricity and chemical costs, not the capital equipment costs. A gas flow rate of 3 million cfm was assumed. Based on a superficial gas velocity of 4.5 ft/s and assuming a diameter of 50 ft for each column, a total of six absorbers columns would be needed to treat the gas. A 10-year equipment life was also assumed. The analysis also seemed to indicate that the tower packing cost much less than the tower shell. However, updated information on packing, shell, and equipment prices were obtained from an outside source and will be used to update the packing analysis and the final results will be presented in the next report. This will aid in the proper selection of packing material for the first campaign. The current default packing is CMR #2.

Results and Discussion (Mass & Energy Balance)

An initial mass and energy balance was performed on the absorber/stripper system for a base case. We anticipate the material and energy balance will be refined as we approach the time for plant start-up. A gas rate of 422 SCFM and liquid rate of 36.8 gpm was used (Table 8). This was based on the previous calculation that gave a pressure drop of approximately 1-inch per foot of packing in the absorber column. The capacity of the solution was assumed to be 0.5 kmol CO₂ per kg of water. The absorber and stripper pressures were assumed to be 1 and 1.4 atm, respectively. A concentration of 12% CO₂ in the gas phase was assumed and it was assumed that 90% removal of the CO₂ occurred in the absorber. The stream results are presented in Table 9 and the corresponding streams are listed in Figure 16. Table 10 lists the equipment specifications and the streams associated with the process streams. The steam rates to the solvent heater and reboiler were calculated to be approximately 700-800 lb/hr (Table 11). The solvent

Table 8. Material & Energy Balance Case Specification

CO ₂	12%
Percent Removal	90%
Capacity	0.5 kmol/kg h2O
Gas Flow (scfm)	422
Liquid Flow (gpm)	36.8
Absorber Pressure	1 atm
Stripper Pressure	1.4 atm

Table 9. Stream Flow Specification

Stream No.	1	2	3	4	5	6	7	8	9	10	11
Stream	Abs Feed	Fd Htr In	Fd Htr Out	Strp Fd	Cooler Fd	Ab Tk Fd	Cnd L Out	Rfix In	Rfix Out	Ab G Out	Blwr In
Temperature (°F)	104.0	140.0	235.7	235.7	235.7	104.0	100.0	100.0	235.7	140.0	130.0
Pressure (atm)	1.0	1.0	1.4	1.4	1.0	1.0	1.4	1.4	1.4	1.0	1.0
Vapor Fraction	0	0	0	0	0	0	0	0	0	1	1
Mass Flow (lb/hr)	21,941	21,898	21,898	22,152	21,941	21,941	254	254	254	1,796	1,987
Vol. Flow (gpm/acfm)	36.8	36.7	36.7	36.8	36.5	36.5	0.5	0.5	0.5	486.0	528.7

Stream No.	12	13	14	15	16	17	18
Stream	Air Clr In	Air Clr Dm	Ab G In	Cnd G Out	ACC Out	Rblr In	Rblr Vapr
Temperature (°F)	140.0	104.0	104.0	100.0	100.0	235.7	235.7
Pressure (atm)	1.0	1.0	1.0	1.3	1.2	1.4	1.4
Vapor Fraction	1	0	1	1	1	0	1
Mass Flow (lb/hr)	1,987	159	1,750	311	311	20,643	839
Vol. Flow (gpm/acfm)	537.6	0.3	505.4	37.1	40.1	34.3	1.4

Table 10. Equipment Specification

Equipment ID No.	Absorber Gas	Absorber Liquid	Stripper Gas	Stripper Liquid	Reboiler H-102	Condenser H-104	Reboiler H-102	Condenser H-104
Stream	Gas	Solvent	Gas	Solvent	Solvent	Gas	Water Vapor	Liquid Water
Duty (Btu/hr)	-	-	-	797290.0596	797,290	-292,256	-	-
Pressure (atm)	1	1	1.4	1.4	1.4	1.4	1.4	1.4
Temp. IN (°F)	104.0	104.0	-	235.7	235.7	216.9	-	-
Temp. OUT(°F)	140.0	140.0	216.9	235.7	235.7	100.0	235.7	100.0
Flow In (lb/hr)	1,750	21,941	-	22,152	20,643	566	-	-
Flow In (gpm/acfm)	505.4	36.8	-	36.8	34.3	124.8	-	-
Flow Out (lb/hr)	1,796	21,898	566	21,941	21,941	311	839	254
Flow Out (gpm/acfm)	486.0	36.7	124.8	36.5	36.5	37.1	1.4	0.5

ID No.	Feed Heater H-101A	Feed Heater H-101B	Solvent Cooler H-107	Cond. Preheatr H-111	Air Cooler H-112
Stream	Rich Solvent	Rich Solvent	Lean Solvent	Water	Rich Gas
Duty (Btu/hr)	791,979	791,979	-2,178,235	34,530	-181,622
Pressure (atm)	1.4	1.4	1.0	1.4	1.0
Temp. IN (°F)	140.0	140.0	235.7	100.0	140.0
Temp. OUT(°F)	235.7	235.7	104.0	235.7	104.0
Flow (lb/hr)	10,949	10,949	21,941	254	53
Flow (acfm)	-	-	-	-	538
Flow (gpm)	18.4	18.4	36.8	0.5	-

Table 11. Utility Specification

Equipment	Feed Htr A	Feed Htr B	Reboiler	Condenser	Solvent Cooler	Reflux Htr	Air Cooler	Total
ID No.	H-101	H-101	H-102	H-104	H-107	H-111	H-112	-
Stream	LPS	LPS	LPS	CW	CW	LPS	CW	-
Duty (Btu/hr)	791,979	791,979	797,290	-292,256	-2,178,235	34,530	-181,622	-
Temp. In (°F)	341.0	341.0	341.0	55.0	55.0	341.0	55.0	-
Temp. Out (°F)	140.1	140.1	245.2	211.3	73.6	100.0	98.5	-
Flow (lb/hr) (Steam)	733.7	733.7	818.3	-	-	30.8	-	2,563
Flow (gpm) (CW)	-	-	-	3.7	234.5	-	8.3	246.6

Note:

LPS - Lower pressure steam, 130 psi

CW - Cooling Water

Figure 16. Stream Designations

cooler would require about 240 gpm of cooling water, while the condenser and air cooler only needed less than 10 gpm each. The total cooling water capacity of the pilot plant is 400 gpm. The proposed base case for the pilot plant will be well within the capacity limits and will permit us to run a wide array of scenarios to optimize the process.

Equipment List

An equipment list with performance and capacity specifications was developed (Table 13). The table lists the physical dimensions and specifications, the materials of construction (MOC), the design temperatures and pressures, and stream flows, where CW = cooling water, STM = steam, G = gas, and L = liquid solvent. Only four of the items are considered to be new additions to the equipment list, which include the two solvent heaters, the solvent cooler, and the air cooler. Table 12 lists the current status for each of the new pieces of equipment.

Table 12. New Equipment Status

New Equipment		Status			
ID	Function	Designed	Ordered	Received	Installed
H-101A	Feed Heater	X	X	X	-
H-101B	Feed Heater	X	X	X	-
H-107	Solvent Cooler	X	X	X	-
H-112	Air Cooler	X	X	-	-

Conclusions

The welding bid will be opened in mid-July and we expect to begin the welding process by the beginning of August and to continue through the end of October. Construction of the 3 skids/rack supports for the solvent heater and solvent cooler will be completed and then installed. The air cooler will be installed, along with the 8-inch PVC piping from the air cooler to the absorber gas inlet. The final design for the process instrumentation and analytical setup will also need to be completed and the associated parts ordered. A top section of the absorber column for the COFLOTM tray will need to be fabricated. The economic analysis of packing materials for the absorber column will also need to be finished. A task plan will be developed and will be submitted 2 months prior to the commencement of the first campaign.

Table 13. Equipment Specification List

Equipment	Function	Status	Equipment Specification				MOC	T _{Dsgn} (°F)	P _{Dsgn} (psig)	Phase
Vessels			Vol (ft³)	Vol (gal)	ID (in)	No. Bed	Bed Ht (ft)			
V-102	Stripper	Existing	-	-	16.8	2	10	CS	400	75 G/L
V-104	Absorber	Existing	-	-	16.8	2	10	CS	350	75 G/L
V-103	OVHD Horiz. Acc.	Existing	85	-	-	-	-	CS	400	75 G
V-105	Absorber Feed Tank	Existing	-	950	-	-	-	CS	450	75 L
V-106	OVHD Liq. Acc.	Existing	-	50	-	-	-	CS	300	75 L
Heat Exchangers			Type	Duty (Btu/hr)	Area (ft²)	Passes		Shell Tube	Shell Tube	Shell Tube
H-101A	Feed Heater	New	Hairpin	800,000	107	1-1		CS 316	650 400	500 500 STM L
H-101B	Feed Heater	New	Hairpin	800,000	107	1-1		CS 316	650 400	500 500 STM L
H-107	Solvent Cooler	New	Fixed	1,720,000	144	1-2		316 316	450 450	225 150 L CW
H-111	Condenser Preheater	Existing	Fixed	220,000	16	1-4		316 316	450 450	225 150 STM L
H-112	Air Cooler	New	Fixed	460,000	213??	-		316 316	- -	- G CW
Condensers/Reboilers			Type	Duty	Area (ft²)	Passes		Shell Tube	Shell Tube	Shell Tube
H-102	Reboiler	Existing	Fixed	2,370,000	200	1-2		CS CS	400 400	100 175 G/L STM
H-104	Condenser	Existing	Fixed	2,350,000	154	1-1		CS CS	300 350	150 150 G/L CW
Pumps			Cap (gpm)	Diff Hd (ft)	Eff. (%)	Type	Power (HP)			
P-102-DI	Stripper Bottoms Pump	Existing	30	195	27	Centrifugal	7.5	CS	350	190 L
P-103-DI	OVHD Acc Pump	Existing	15	200	15	Centrifugal	7.5	CS	350	190 L
P-104-DI	Absorber Pump	Existing	100	120	59	Centrifugal	7.5	CS	350	240 L
P-105-DI	Absorber Pump	Existing	15	120	16	Centrifugal	5	CS	350	240 L

P-106-DI	Absorber Feed Pump	Existing	50	135	42.5	Centrifugal	5	CS	350	240	L
Blower/Vacuum Pump											
C-102A	Vacuum Pump	Existing	430	15			15	CS	-	10	G
C-103	Blower	Existing	1500	3			40	CS	1200	5	G

References

1. Cullinane, J. T. (2002). Carbon Dioxide Absorption in Aqueous Mixtures of Potassium Carbonate and Piperazine. M.S. Thesis, The University of Texas at Austin, Austin, Texas.
2. Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. (1982). "Local Composition Model for Excess Gibbs Energy of Electrolyte Systems. Part I: Single Solvent, Single Completely Dissociated Electrolyte Systems." *AIChE J.* **28**(4): 588-96.
3. Renon, H.; Prausnitz, J. M. (1968). "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures." *AIChE J.* **14**(1): 135-44.
4. Austgen, D. M. (1989). A Model of Vapor-Liquid Equilibria For Acid Gas-Alkanolamine-Water Systems. Ph.D. Dissertation, The University of Texas at Austin, Austin, Texas.
5. Posey, M. L. (1996). Thermodynamic Model for Acid Gas Loaded Aqueous Alkanolamine Solutions. Ph.D. Dissertation, The University of Texas at Austin, Austin, Texas.
6. Edwards, T. J.; Maurer, G.; Newman, J.; Prausnitz, J. M. (1978). "Vapor-Liquid Equilibria in Multicomponent Aqueous Solutions of Volatile Weak Electrolytes." *AIChE J.* **24**(6): 966-76.
7. Bishnoi, S. (2000). Carbon Dioxide Absorption and Solution Equilibrium in Piperazine. The University of Texas at Austin. Ph.D. Dissertation, Austin, Texas.
8. Caracotsios, M. (1986). Model Parametric Sensitivity Analysis and Nonlinear Parameter Estimation: Theory and Applications. Ph.D. Dissertation, The University of Wisconsin. Madison, Wisconsin.
9. Gmehling, J.; Li, J.; Schiller, M. (1993). "A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties." *Industrial & Engineering Chemistry Research* **32**(1): 178-93.
10. Puchkov, L. V.; Kurochkina, V. V. (1970). "Vapor Pressure of Aqueous Potassium Carbonate Solutions." *Zhurnal Prikladnoi Khimii (Sankt-Peterburg, Russian Federation)* **43**(1): 181-3.
11. Apelblat, A. (1992). "The Vapor Pressures of Water over Saturated Aqueous Solutions of Barium Chloride, Magnesium Nitrate, Calcium Nitrate, Potassium Carbonate, and Zinc Sulfate, at Temperatures from 283 K to 313 K." *Journal of Chemical Thermodynamics* **24**(6): 619-26.
12. Aseyev, G. G. (1999). "Electrolytes: Equilibria in Solutions and Phase Equilibria. Calculation of Multicomponent Systems and Experimental Data on the Activities of Water, Vapor Pressures, and Osmotic Coefficients". New York, Begell House.
13. Sarbar, M.; Covington, A. K.; Nuttall, R. L.; Goldberg, R. N. (1982). "Activity and Osmotic Coefficients of Aqueous Potassium Carbonate." *Journal of Chemical Thermodynamics* **14**(7): 695-702.
14. Roy, R. N.; Gibbons, J. J.; Williams, R.; Godwin, L.; Baker, G.; Simonson, J. M.; Pitzer, K. S. (1984). "The Thermodynamics of Aqueous Carbonate Solutions. II.

- Mixtures of Potassium Carbonate, Bicarbonate, and Chloride.” *Journal of Chemical Thermodynamics* **16**(4): 303-15.
15. Simonson, J. M.; Roy, R. N.; Gibbons, J. J. (1987). “Thermodynamics of Aqueous Mixed Potassium Carbonate, Bicarbonate, and Chloride Solutions to 368 K.” *Journal of Chemical and Engineering Data* **32**(1): 41-5.
 16. Tosh, J. S.; Field, J. H.; Benson, H. E.; Haynes, W. P. (1959). “Equilibrium Study of the System Potassium Carbonate, Potassium Bicarbonate, Carbon Dioxide, and Water.” *U.S. Bur. Mines, Rept. Invest. No. 5484*: 23 pp.
 17. Kamps, A. P.; Xia, J.; Maurer, G. (2003). “Solubility of CO₂ in (H₂O + Piperazine) and in (H₂O + MDEA + Piperazine).” *Submitted to AIChE J.*
 18. Ermatchkov, V.; Kamps, A. P.-S.; Maurer, G. (2002). “Chemical Equilibrium Constants for the Formation of Carbamates in the System CO₂+Piperazine+Water From ¹H-NMR Spectroscopy.” *J. Chem. Thermodyn. (in press)*.
 19. Markham, A. E.; Kobe, K. A. (1941). “The Solubility of Carbon Dioxide and Nitrous Oxide in Aqueous Salt Solutions.” *Journal of the American Chemical Society* **63**: 449-54.
 20. Joosten, G. E. H.; Danckwerts, P. V. (1972). “Solubility and Diffusivity of Nitrous Oxide in Equimolar Potassium Carbonate-Potassium Bicarbonate Solutions at 25 Deg. and 1 Atm.” *Journal of Chemical and Engineering Data* **17**(4): 452-4.
 21. Schumpe, A. (1993). “The Estimation of Gas Solubilities in Salt Solutions.” *Chemical Engineering Science* **48**(1): 153-8.
 22. Aspen Technology. *Aspen Plus: Getting Started Modeling Processes with Electrolytes Version 11.1*. Cambridge: Author.
 23. Bishnoi, S.; Rochelle, G. T. (2000) “Absorption of Carbon Dioxide into Aqueous Piperazine: Reaction Kinetics, Mass Transfer, and Solubility.” *Chemical Engineering Science*, 55(22), 5531-5543.
 24. Cullinane, J. T.; Rochelle, G. T. (2003) “Properties of Concentrated Aqueous Potassium Carbonate/Piperazine for CO₂ Capture, ” presented at the 2nd Annual Conference on Carbon Sequestration, Alexandria, Virginia.
 25. Aspen Custom Modeler Manual.
 26. Dang, H. (2001) CO₂ Absorption Rate and Solubility in Monoethanolamine/Piperazine/Water. M.S. Thesis, The University of Texas at Austin, Austin, TX.
 27. Onda, K.; Takeuchi, H.; Okumoto, Y. (1968) “Mass transfer coefficients between gas and liquid phases in packed columns”, *Journal of Chemical engineering of Japan*, 1(1).
 28. Wilson, Ian. (2003) Gas-Liquid Contact Area of Random and Structure Packing. Quarterly Progress Report, April 1-June 30, 2003.
 29. Freguia, S. (2002) Modeling of CO₂ Removal from Flue Gases with Monoethanolamine. M.S. Thesis, The University of Texas at Austin, Austin, TX.