CO$_2$ Capture by Absorption with Potassium Carbonate

Quarterly Progress Report
Reporting Period Start Date: July 1, 2003
Reporting Period End Date: September 30, 2003
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October 31, 2003
DOE Award #: DE-FC26-02NT41440
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Abstract

The objective of this work is to improve the process for CO_2 capture by alkanolamine absorption/stripping by developing an alternative solvent, aqueous K_2CO_3 promoted by piperazine. A rigorous thermodynamic model has been further developed with a stand-alone FORTRAN code to represent the CO_2 vapor pressure and speciation of the new solvent. The welding work has initiated and will be completed for a revised startup of the pilot plant in Feburary 2004.

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Introduction

The objective of this work is to improve the process for CO_2 capture by alkanolamine absorption/stripping by developing an alternative solvent, aqueous K_2CO_3 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 for direct effort on the scope of this contract.

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 final set of parameters for the stand-alone FORTRAN model.

Marcus Hilliard has obtained salt/water parameters for potassium carbonate in the Aspen model.

Subtask 1.3 – Develop Integrated Absorber/Stripper Model

Babatunde Oyenekan has developed algebraic representation of VLE to be use in a mathematical framework to simulate a stripper with Aspen Custom Modeler.

Subtask 2.1 – Pilot Plant Test Plan

Eric Chen has prepared a draft test plan for the first campaign.

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

Eric Chen has updated the schedule for the pilot plant modification. Welding of piping modifications has begun.

Conclusions

1. The stand-alone NRTL electrolyte model with regressed parameters is robust and represents liquid speciation and VLE predictions of K^+/CO_2 systems, PZ-CO_2 systems, and mixed solvent systems from 25 to 80^oC. Over identical P_{CO2}* ranges, the addition of K^+ to PZ yields more reactive species. Free PZ is sacrificed for PZCOO$^-$, but the total amount of reactive PZ increases due to reduced protonation with the addition of the CO_3/HCO_3 buffer.

2. Regression of data for the Aspen Electrolyte-NRTL model indicates that it will use parameters different from those in the stand-alone FORTRAN model.

3. The absorber stripper pilot plant is scheduled to start shakedown in February 2003.

Future Work

We expect the following accomplishments in the next quarter:

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

An initial set of parameters will be developed for the Aspen model.

Subtask 1.3 – Develop Integrated Absorber/Stripper Model

A simple excel spreadsheet model will be developed for the absorber and the stripper to be used in the first pilot plant campaign.

Subtask 2.1 – Pilot Plant Test Plan

The detailed test plan for the first campaign will be submitted for approval.

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

Piping modifications and equipment installation will be completed. Pilot plant start-up is now scheduled for February 2004.

Task 1 – Modeling Performance of Absorption/Stripping of CO_2 with Aqueous K_2CO_3 Promoted by Piperazine

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

by J. Tim Cullinane

Introduction

This report presents the continuing development of aqueous potassium carbonate-piperazine mixtures for CO_2 removal from flue gas.

As previous reports have indicated, data on CO_2 partial pressure, piperazine speciation, and CO_2 absorption rates have been collected (Cullinane 2002). The most recent report detailed the continuing development of a thermodynamic model capable of predicting speciation and vapor pressures in K^+/PZ solutions. Also, physical solubility data was shown for a significant concentration range. It was found that PZ had little effect on gas solubility. Correlations for gas solubility in K_2CO_3 and $KHCO_3$ solutions are suitable for modeling.

The equilibrium model has been modified from previous versions. PZ-water interactions were based on UNIFAC predictions. This allowed a reduction in the number of τ parameters used for PZ species, simplifying the model and improving statistical regressions. Additionally, interaction parameters for CO_2 were added, allowing the modeling of CO_2 activity coefficients garnered from physical solubility measurements.

In addition to thermodynamic modeling, investigations into CO_2 absorption in aqueous PZ were begun. Current data suggests that CO_2 is absorbed through a "zwitterion" mechanism which is second order with respect to PZ.

Experimental

The thermodynamic model used is the electrolyte Non-Random Two-Liquid model (electrolyte NRTL) developed by Chen et al. (1982) 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 (Renon and Prausnitz 1968). 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 (1989) and Posey (1996).

In the model used in this work, all molecule-molecule and ion pair-ion pair parameters are set to zero, unless otherwise noted. 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**	
$K_{HCO_3^-} = \dfrac{x_{HCO_3^-} \cdot x_{H_3O^+}}{x_{CO_2} \cdot x_{H_2O}^2}$	231.4	-12092	-36.78	Posey (1996) Edwards (1978)
$K_{CO_3^{2-}} = \dfrac{x_{H_3O^+} \cdot x_{CO_3^{2-}}}{x_{HCO_3^-} \cdot x_{H_2O}}$	216.0	-12432	-35.48	Posey (1996) Edwards (1978)
$K_w = \dfrac{x_{H_3O^+} \cdot x_{OH^-}}{x_{H_2O}^2}$	132.9	-13446	-22.48	Posey (1996) Edwards (1978)
$K_{PZH^+} = \dfrac{x_{PZ} \cdot x_{H_3O^+}}{x_{PZH^+} \cdot x_{H_2O}}$	4.964	-9714	0.0	Bishnoi (2000)
$K_{PZCOO^-} = \dfrac{x_{PZCOO^-} \cdot x_{H_3O^+}}{x_{PZ} \cdot x_{CO_2} \cdot x_{H_2O}}$	-47.05	11268	0.0	This Work

$K_{H^+PZCOO^-} = \dfrac{x_{PZCOO^-} \cdot x_{H_3O^+}}{x_{H^+PZCOO^-} \cdot x_{H_2O}}$	-22.65	-680	0.0	This Work
$K_{PZ(COO^-)_2} = \dfrac{x_{PZ(COO^-)_2} \cdot x_{H_3O^+}}{x_{PZCOO^-} \cdot x_{CO_2} \cdot x_{H_2O}}$	-14.96	380	0.0	This Work

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

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

A wetted-wall column was used as a gas-liquid contactor to measure P_{CO2}^* and CO_2 absorption rates. The equipment, shown in the schematic in Figure 1, has been used most recently in the work of Bishnoi (2000). The column itself is a stainless steel tube, measuring 9.1 cm in height and 1.26 cm in diameter (38.5 cm^2 total area based on the liquid film). The gas-liquid contact region is enclosed by a 2.54 cm OD thick-walled glass tube. A circulating bath of oil, enclosed by a 10.16 cm OD glass annulus, insulates the column from ambient conditions.
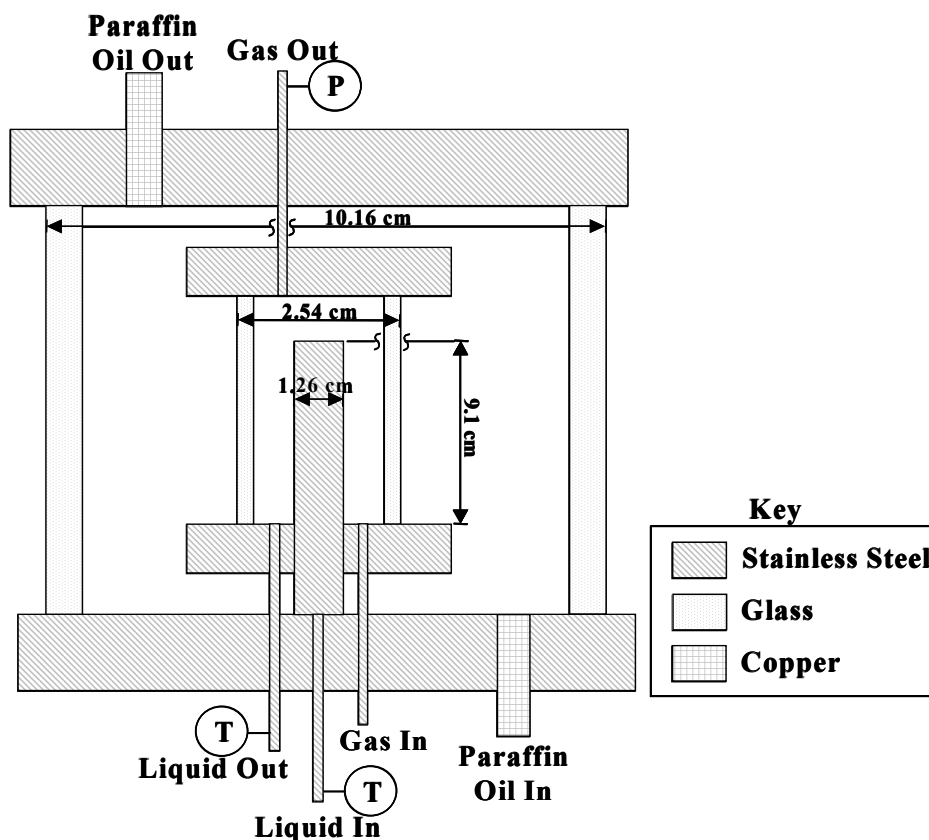
Figure 1. Schematic of the Wetted-Wall Column

The chemical solvent was contained in a 1000 mL reservoir constructed from a modified gas cell. A pump pushes the solution through a coil in a heated circulator. The solution is then pumped through the inside of the wetted-wall column, overflowing, and evenly distributing over the surface. The liquid is collected and pumped back to a liquid reservoir.

A 20 SLPM mass flow controller was used to meter nitrogen flow. The carbon dioxide flowrate was metered with a 1 or 2 SLPM mass flow controller depending on the desired concentration ranges. The metered gases were mixed and saturated with water in a calorimetric bomb heated in an oil bath. The gas flows through the gas-liquid contact region and absorbs or desorbs CO_2. After exiting the column, the gas is dried in a condenser and a drying column. The outlet CO_2 concentration was measured using an IR carbon dioxide analyzer.

The inlet gas flowrate and the outlet gas flowrate provide the necessary information to calculate the flux of CO_2 into, or out of, the solvent. The partial pressure of carbon dioxide was varied, giving both absorption and desorption conditions. From this, an equilibrium partial pressure was interpolated. Liquid samples were taken from the wetted-wall column at steady state conditions. The samples were analyzed for total CO_2 concentration using an IR CO_2 analyzer giving a CO_2 loading.

Results and Discussion

The goal in creating an equilibrium model was the development of a thermodynamically consistent representation of experimental data, capable of providing accurate results over a broad range of concentration and temperature ranges. To this end, the model development was carried out sequentially, as described below. First, thermodynamic information for simpler systems was developed and modeled. Using the base systems as a foundation, the model was expanded to include mixed solvent information. 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 thermodynamically consistent model. Parameter regression was aided by the use of a non-linear regression program named GREG (Caracotsios 1986). 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_2O, K^+, CO_3^{2-}	9.27	0.18	1466.5	588.5	**10.04**
	K^+, CO_3^{2-}, H_2O	-4.49	0.04	-344.6	113.7	**-4.67**
2	H_2O, K^+, HCO_3^-	7.61	0.04	3246.2	Indet.*	**9.31**
	K^+, HCO_3^-, H_2O	-3.37	Indet.*	-763.2	78.6	**-3.77**
3	H_2O, PZ	1.67	0.42	Def.**	-	**1.67**
	PZ, H_2O	10.10	0.25	-3606.3	Indet.*	**-2.00**
4/6	H_2O, PZH^+, HCO_3^-	8.62	0.28	Def.**	-	**8.62**
	PZH^+, $PZCOO^-$, H_2O	-5.44	0.61	Def.**	-	**-5.44**
	H_2O, PZH^+, $PZ(COO^-)_2$	Def.**	-	-1714.7	2667.6	**7.10**
5/6	H_2O, K^+, $PZCOO^-$	10.32	0.44	-5570.4	1662.9	**7.41**
	H_2O, K^+, $PZ(COO^-)_2$	7.74	0.45	-2002.5	1252.7	**6.69**
	H_2O, PZH^+, CO_3^-	7.66	2.04	Def.**	-	**7.66**
	H_2O, PZH^+, $PZ(COO^-)_2$	5.66	1.09	Def.**	-	**5.66**
7***	K^+, CO_3^{2-}, CO_2	-9.62	0.12	8431.4	Indet.*	**-5.22**
	K^+, HCO_3^-, CO_2	-1.24	Indet.*	-7089.4	911.7	**-4.94**
	K^+, $PZ(COO^-)_2$, CO_2	5.64	0.51	Def.**	-	**5.64**

* Indeterminate: Represents a high correlation between parameters.

** Default parameters used.

*** In progress

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In the first 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 available resulting in a wide range of temperatures, 25 to 120°C, and concentration, 0 to 50 wt% K_2CO_3 (Puchkov and Kurochkina 1970). The values of four regressed parameters are consistent with other salt solutions as reported by Chen et al. (1982).

The second set of regressed parameters describes $KHCO_3$ behavior as interpreted from VLE data by Tosh et al. (1959). A normalized parity plot of the predicted CO_2 partial pressures is shown in Figure 2. 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%.

With the first two steps complete, the model is applicable to low pressure K^+, CO_2, H_2O systems over a wide range of temperatures.

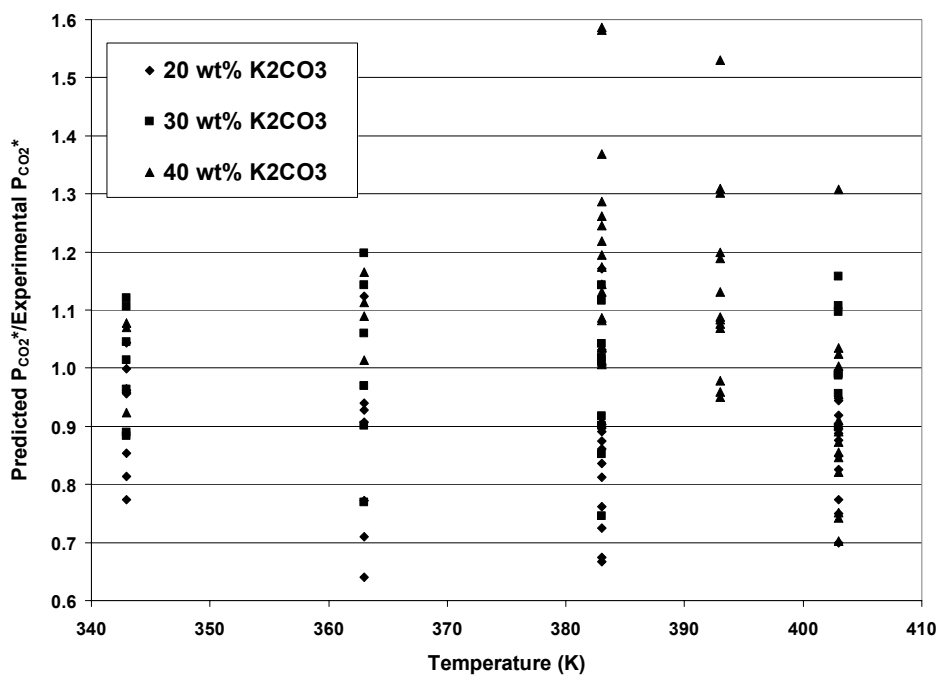**Figure 2. Electrolyte NRTL Model Predictions of CO$_2$ Vapor Pressure in Aqueous Potassium Carbonate Solutions (Tosh *et al.*, 1959) Using Parameters Shown in Table 1**

The third step defines the infinite dilution activity coefficient of piperazine in water. Predictions of the UNIFAC thermodynamic model (Gmehling et al. 1993) were assumed accurate for compositions from 0.1 to ~1.8 m (the solid solubility at 25°C) and

temperatures ranging from 25 to 50°C. The parameters in the electrolyte NRTL model were adjusted to fit UNIFAC predictions.

The fourth step utilized proton (^{1}H) NMR data for speciation of loaded piperazine solutions and total pressure data over similar solutions as reported by Kamps et al. (2003) and Ermatchkov et al. (2002). Additional vapor pressure data was found in Bishnoi (2000).

After the forth step, the model can predict speciation and VLE in both K^+, CO_2, H_2O systems and PZ, CO_2, H_2O systems without further modification.

The fifth regression in the sequence utilized past (Cullinane 2002) and current ^{1}H 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.

After a fifth regression gave preliminary τ parameters for the mixed solvent system, it was deemed necessary to return and include all relevant parameters for PZ and K^+/PZ speciation in one large regression (Step 6). This enabled elimination of several τ parameters and refined the model predictions for the available data sets.

The seventh, and final, step in the regression sequence includes CO_2 activity data obtained from previously reported physical solubility experiments. Though still in progress, this step enables accurate prediction of CO_2 solubility in solution and will allow for more physically significant conclusions to be drawn concerning the kinetics of the reaction, which will be examined in the near future.

The completed model was used to speciate concentrated PZ systems to identify the effect of salt addition. Predictions were made in two solutions: 1.8 m PZ (Figure 3) and 3.6 m K^+/1.8 m PZ (Figure 4). The speciation of the aqueous amine solution shows that as CO_2 is absorbed, much of the reactants are consumed by protonation. At high P_{CO_2}* the protonated species are the dominant forms of the amine. From this prediction, it is expected (and has been observed experimentally) that highly loaded solutions react slower due to the loss of reactive amine.

The addition of 3.6 m K^+ to the 1.8 m PZ solution dramatically affects the speciation over the same partial pressure range. This solution sacrifices free PZ for PZCOO$^-$ and PZ(COO$^-$)$_2$, but the total amount of reactive species is higher than that of an aqueous PZ solution. Because piperazine carbamate is still reactive with CO_2, this solution maintains a fast absorption rate. Note that the amine in the salt solution is not as readily protonated as the mixture is still buffered by the high concentration of carbonate/bicarbonate.

From the wetted-wall column, data covering broad concentration ranges of the mixed solvent (0 to 6.2 m K+ and 0 to 3.6 m PZ) have been previously obtained. These data suggest a promotion of the reaction rate in the presence of K_2CO_3. It is unclear if the rate increase is a result of ionic strength effects or additional proton withdrawing in the zwitterion mechanism.

The zwitterion mechanism is generally accepted as the mechanism for CO_2 absorption by primary and secondary amines. It is a two step process in which the CO_2 and amine react to form a zwitterion intermediate followed by deprotonation by a base such as the free amine or water.
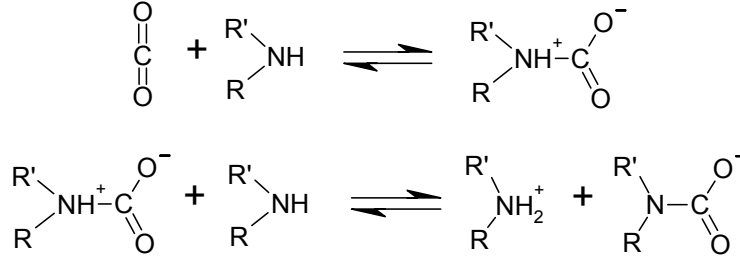
The suggested form of the rate of reaction can be written as

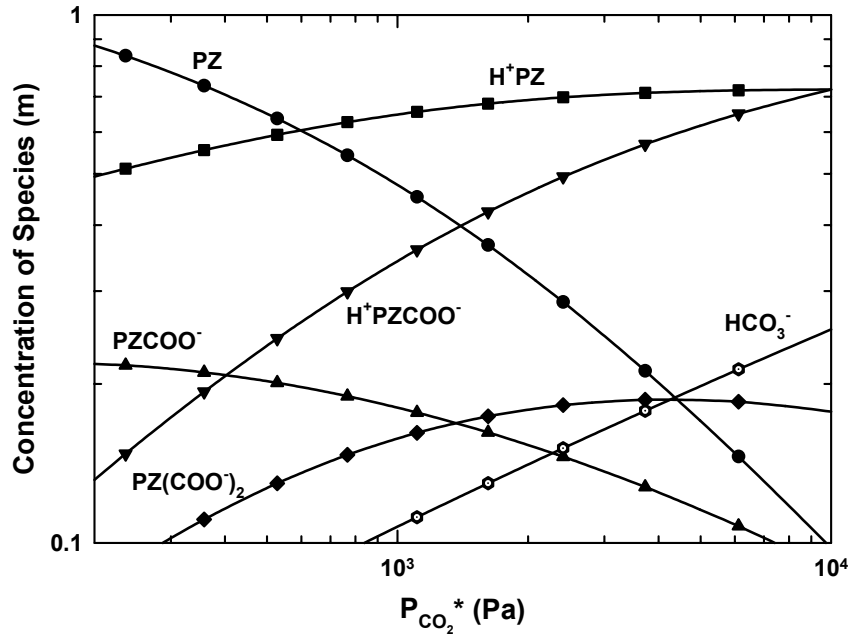$$r = \frac{k_f[CO_2][Am]}{1 + \dfrac{k_r}{\sum k_b[B]}}$$

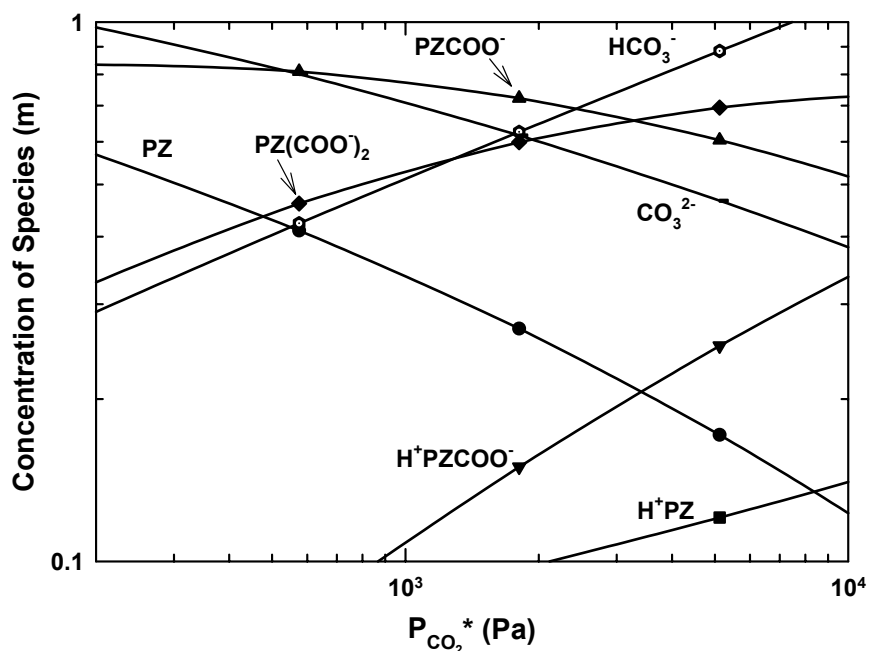**Figure 3. Speciation in 1.8 m PZ at 40°C**

Figure 4. Speciation in 3.6 m K$^+$/1.8 m PZ at 40°C

When deprotonation of the zwitterion is rate determining, the contribution of the bases to the rate, $\Sigma k_b[B]$, is small and the denominator must be considered. When the formation of the zwitterion is rate controlling, $\Sigma k_b[B]$ is large and the mechanism reduces to first order with respect to the amine and second order overall.

In an effort to clarify the reaction mechanism for PZ, absorption rates in varying concentrations of aqueous PZ have been measured. The results are shown in Figure 5. Data on aqueous PZ (0.2 and 0.6 m) had been obtained previously by Bishnoi (2000). The apparent k_2 was evaluated using the following expression for pseudo-first order reaction.

$$N_{CO_2} = \frac{\sqrt{D_{CO_2} k_2 [PZ]}}{H} P_{CO_2,\text{int}}$$

The results demonstrate an apparent rate constant that has a linear dependence on piperazine concentration. This indicates a reaction mechanism that is second order with respect to the amine, suggesting that CO_2 reacting with PZ follows a zwitterion mechanism where the proton extraction is rate limiting. Furthermore, it can be stated that PZ is the major proton withdrawing group.

These results lend credence to the theory that rate promotion in mixed solvents is a result of zwitterion enhancement. Carbonate is expected to be a strong proton withdrawing group, possibly promoting the absorption rate. Still, contribution from ionic strength effects cannot be ruled out.
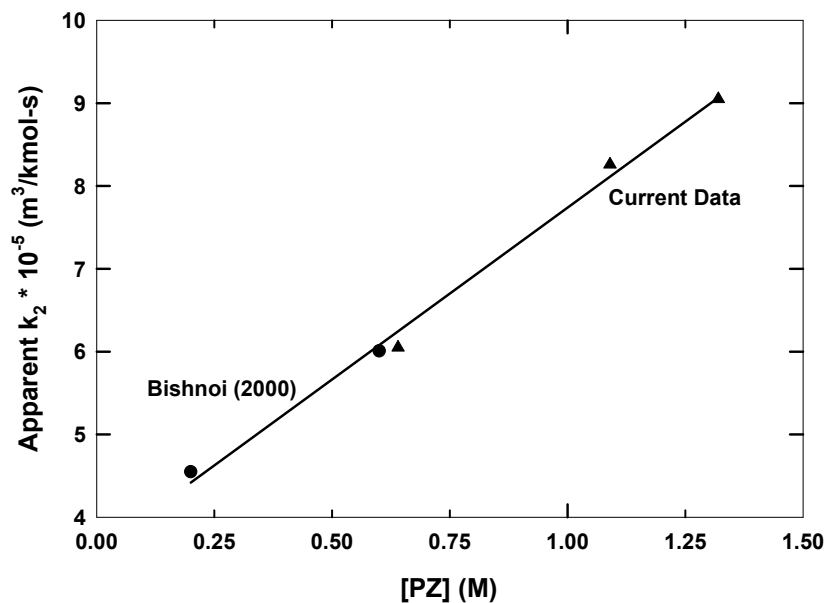
Figure 5. Apparent Rate Constant for the Reaction of CO_2 with PZ at 25°C

Conclusions

A rigorous thermodynamic model, using the electrolyte NRTL theory, has been developed for use with solutions containing K^+ and PZ. The model is robust, enabling liquid speciation and VLE predictions of K^+/CO_2 systems, PZ-CO_2 systems, and mixed solvent systems from 25 to 80°C.

Predictions from the thermodynamic model indicate practical advantages in promoting PZ solutions with K^+. Over identical $P_{CO2}*$ ranges, the addition of K^+ to PZ yields more reactive species. Free PZ is sacrificed for PZCOO$^-$, but the total amount of reactive PZ increases due to reduced protonation with the addition of the CO_3/HCO_3 buffer.

The mechanism of the CO_2-PZ reaction appears to be zwitterion with the proton extraction being the rate limiting step. In aqueous PZ, PZ is the major withdrawing species while water, although likely making small contributions to rate, has no discernable role. This conclusion leads to the expectation that, in mixed solvents, carbonate will enhance CO_2 absorption by adding to the proton withdrawing effect.

Future work will focus on finalizing the thermodynamic model and incorporating it into a rigorous rate model. The rate model will allow predictions of the rate of CO_2 absorption in mixed solvent systems. By adjustment of the rate expression and specific rate constants, a kinetic mechanism may be inferable and quantifiable.

In addition to the continuing development of the reaction kinetics, solvent behavior in the stripper will be examined. The wetted-wall column will be run at high temperatures (80 to 120°C), typical of stripper conditions. The ensuing data will contribute to the current VLE database and help elucidate mass transfer processes.

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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 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 the use of previous models in the integrated simulation.

Previously, 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. 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 required further study.

A rigorous thermodynamic model is now being developed to predict the equilibrium and speciation in potassium carbonate/piperazine mixtures for future use in process modeling. The model integrated into the structure of Aspen Plus™ utilizes the electrolyte NRTL model that was originally proposed by Chen et al. (1982) for aqueous electrolyte systems and later was extended to mixed solvent electrolyte systems by Mock et al. Using binary and pair parameters, the model can represent aqueous electrolyte systems as well as mixed solvent electrolyte systems over the entire range of electrolyte concentrations. This model can calculate activity coefficients for ionic species and molecular species in aqueous electrolyte systems as well as in mixed solvent electrolyte systems. The electrolyte NTRL model uses the infinite dilution aqueous solution as the reference state for ions and adopts the Born equation to account for the transformation of the reference state of ions from the infinite dilution mixed solvent solution to the infinite dilution aqueous solution.

Experimental (Equilibrium Modeling)

Previous work in modeling the potassium carbonate/piperazine mixtures focused on the development of a simple model to describe equilibrium behavior. A simple model was not capable of approximating the correct behavior of this system, but a more thermodynamically rigorous model is desirable for describing the complex solution characteristics for future process models.

The electrolyte NRTL model is a versatile model for the calculation of activity coefficients. The model is based on two fundamental assumptions:

1. ***The like-ion repulsion assumption:*** states that the local composition of cations around cations is zero (and likewise for anions around anions).

This assumption is based on the fact that the repulsive forces between ions of like charge are extremely large and that the basis that repulsive forces between ions of the same sign are very strong for neighboring species.

2. **The local electroneutrality assumption:** states that the distribution of cations and anions around a central molecular species is such that the net local ionic charge is zero. Local electroneutrality has been observed for interstitial molecules in salt crystals.

Chen et al. (1982) proposed an excess Gibbs energy expression which contains two contributions: one contribution for the long-range ion-ion interactions and the other related to the local interactions that exist around any central species.

The unsymmetric Pitzer-Debije-Hückel (*PDH*) model and the Born equation are used to represent the contribution of the long-range ion-ion interactions, and the NRTL theory was used to represent the local interactions (*lc*). The local interactions model was developed as a symmetric model with a reference state based on pure solvent and pure completely dissociated liquid electrolyte. Infinite dilution activity coefficients then normalized the model by obtaining an un-symmetric model. The NRTL expression for the local interactions, the Pitzer-Debije-Hückel expression, and the Born equation are added to give equation 1 for the excess Gibbs energy.

$$\frac{G_m^{*E}}{RT} = \frac{G_m^{*E,PDH}}{RT} + \frac{G_m^{*E,Born}}{RT} + \frac{G_m^{*E,lc}}{RT} \tag{1}$$

The excess free energy is related to the activity coefficient by the following thermodynamic relationship.

$$\ln \gamma_i = \frac{G_m^{*E}}{RT} \tag{2}$$

This leads to

$$\ln \gamma_i^* = \ln \gamma_i^{*,PDH} + \ln \gamma_i^{*,Born} + \ln \gamma_i^{*,lc} \tag{3}$$

Electrolyte NRTL pair parameters (GMELCC) in Aspen Plus™ 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 3.

Table 3. Default Binary Interaction Parameters for the Electrolyte NRTL Model

Interactions	Value
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

Equilibrium constants used are those found in Posey (1996) and Bishnoi and Rochelle (2000). A more thorough discussion of electrolyte NRTL theory as it pertains to Aspen Plus™ can be found in Physical Property Methods and Models 11.1 (2001).

Results and Discussion

To develop a working model of potassium carbonate/piperazine mixtures, τ must be found for significant contributing species. To simplify the analysis, τ's will be regressed sequentially for several independent data sets to reduce the number of simultaneously regressed parameters. Please refer to Table 4.

Table 4. Sequential Regression Strategy
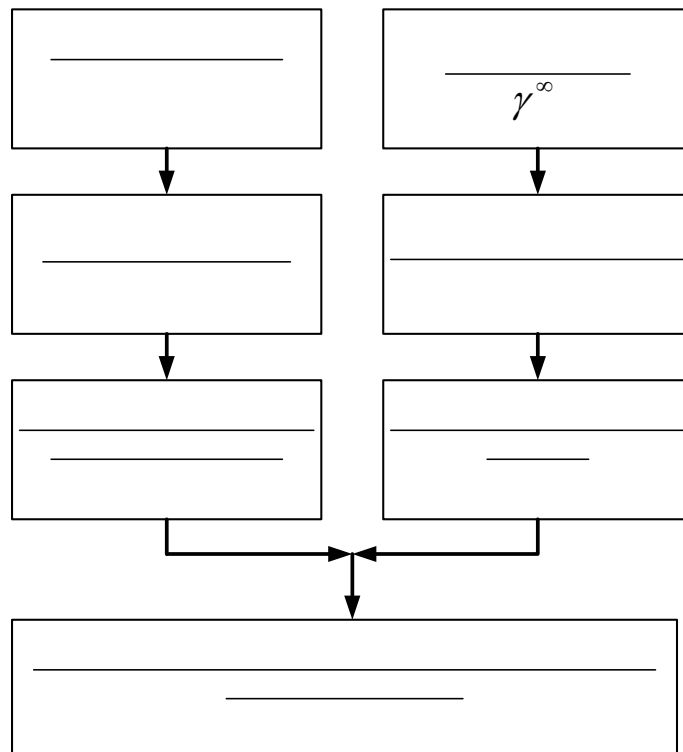
The form used for binary interaction parameters used within Aspen Plus is

$$\tau_{Aspen} = A + \frac{B}{T} + C\left[\frac{\left(T^{ref} - T\right)}{T} + \ln\left(\frac{T}{T^{ref}}\right)\right] \tag{4}$$

where $T^{ref} = 298.15K$. For this model, the C parameter was set to zero.

For the first step in the sequential regression, regressed tau parameters for potassium carbonate/water system were adjusted to fit data for the activity of water in K_2CO_3-water mixtures as calculated from osmotic coefficients, boiling point elevation and mean ionic activity coefficients, and vapor pressure reported by Sarbar (1981), Zaytsev and Aseyev (1999) and Aseyev (1999) respectively. The data provides a wide range of both temperature (235 to 393 K) and concentration (0.0 to 50 wt% K_2CO_3). The data was reduced to cover range in temperature (298 to 393 K) and concentration (14 to 36% K_2CO_3) to describe absorber/stripper conditions.

Parameters were regressed using Aspen Plus build-in regression software that uses a "maximum likelihood method". Maximum likelihood method assumes that all experimental data are not error free and requires users to define the accuracy of the measurements via standard deviations. The maximum likelihood method then puts regressed parameters as close to the data points as the accuracy of the data warrants by minimizing the weighted sum of squares objective function.

The values of four regressed parameters as well as their standard deviations are shown in Table 5.

Table 5. Regressed Binary Interaction Parameters for the Aspen Plus™ ELECNRTL Model

i	j	k	A	σ_A	B	σ_B	τ,298.15 K
H2O	K^+	CO_3^{-2}	7.38	0.88	366.69	292.48	8.61
K^+	CO_3^{-2}	H2O	-4.06	0.31	-73.95	104.17	-4.31

With the regressed parameters, the model predicts the activity of water within 0.73% of the literature values as shown below in Figure 6.
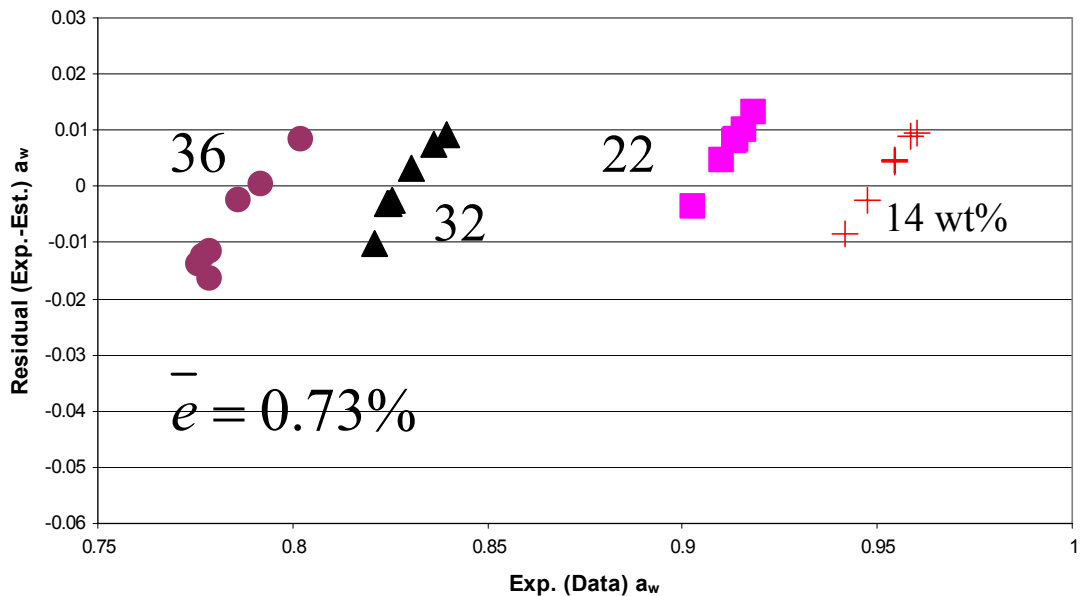
Figure 6. K2CO3 Activity of Water calculated by Parameters Regressed in Aspen (25 to 120°C)

Cullinane and Rochelle (2003) reported the following regressed parameters shown in Table 6.

Table 6. Cullinane Regressed Binary Interaction Parameters for the Electrolyte NRTL Model

i	j	k	A	σ_A	B	σ_B	τ,298.15 K
H2O	K^+	CO_3^{-2}	8.65	0.16	861	371	9.10
K^+	CO_3^{-2}	H2O	-4.30	0.03	-216	75	-4.41

Cullinane reported that the above parameters predict the activity coefficient of water within 2% of the values given in the literature. His parameters were then tested within our Aspen model under the following conditions:

- potassium carbonate concentrations of 14, 22, 32, and 36 wt%
- 25 – 120°C

and agreed with his findings as shown below in Figure 7.
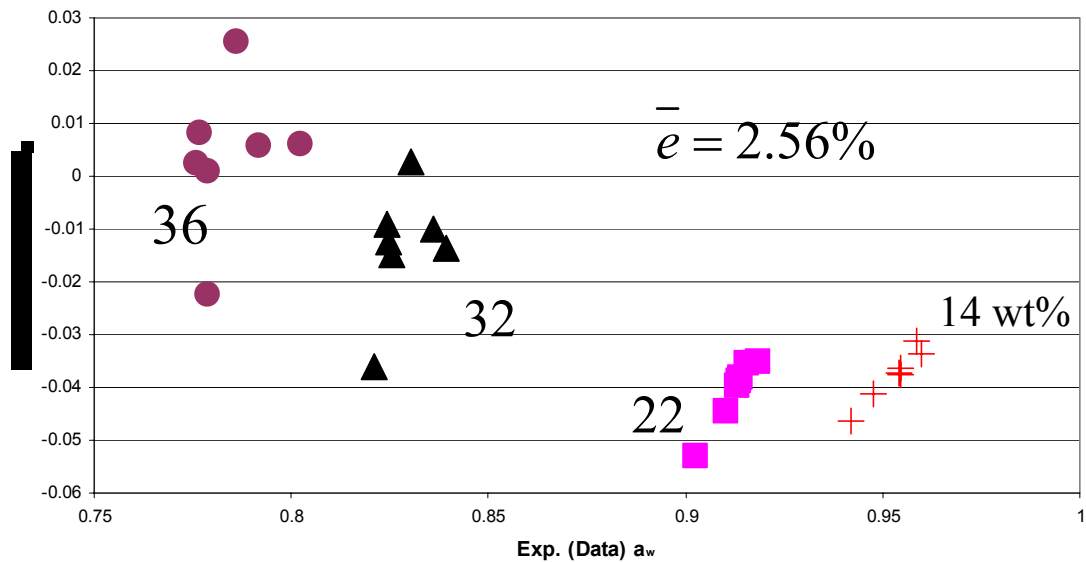
Figure 7. K_2CO_3 Activity of Water Calculated by Cullinane's Parameters in Aspen (25 to 120°C)

Conclusions

Interaction parameters regressed by Cullinane (2002) adequately described the interactions associated with the potassium carbonate/water system and are comparable to those given in this work.

Future Work

The next step in the regression strategy will be to complete the regression of the parameters describing the $KHCO_3$ behavior from mean ionic activity coefficient and partial pressure of water data. Then to test the model against a mixed solvent system of potassium carbonate/potassium bicarbonate by Tosh et al. (1959) and future regression cases will characterize the equilibrium reactions associated with the piperazine speciation. Then the model will be combined with a rigorous rate code developed by Bishnoi (2000) for kinetic parameter regression analysis to model the absorption of CO_2 in potassium carbonate/piperazine systems.

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

by Babatunde Oyenekan
(Supported by this contract)

Introduction

We have continued to develop the stripper submodel in Aspen Custom Modeler (ACM) for an overall model of CO_2 absorption/stripping by an aqueous solution of potassium carbonate and piperazine. This quarter, the equations to be used in the model were revised to improve its flexibility so that different process configurations (simple, vacuum and multi-pressure) can be modelled. A correlation for the equilibrium partial pressure of CO_2 as a function of temperature and loading was developed.

Experimental (Model Formulation)

Modeling Environment

We have an existing MEA stripper model in Aspen RateFrac^{TM} but this cannot be used to model the stripper as Aspen RateFrac^{TM} uses instantaneous reactions to model the reactions in the stripper. This may not be the case especially for vacuum strippers in which the reactions occur at finite rates. Therefore, the current model is not always robust and the approach used by Freguia (2002) for the absorber will not work for the stripper. In order to overcome the above limitations, we have decided to use ACM which uses equation–based models and is compatible as a block in Aspen Plus which is the environment that we would use for the integrated absorber/stripper model. The powerful numerical solvers that are inherent in ACM facilitate the solving of a set of algebraic, ordinary and partial differential equations simultaneously. Aspen Custom Modeler possesses a flexible flowsheet and affords us a great deal of flexibility when modelling mass transfer with chemical reaction. These features reduce the computation time for the simulation and make the model more robust.

Stripper Problem

A review of the literature regarding absorber/stripper operations reveals that most of the time the absorber is modelled without the stripper. The models for absorbers cannot be transferred for use in the strippers because we have to account for the reversibility of the reactions. A significant percentage of the operating cost of an absorber/stripper system is stripping steam. In an effort to reduce energy consumption, the modelling of the stripper should be done. This would have an impact on the work that can be extracted from the turbines in the power plant and hence aid energy integration. Finally, construction of strippers has been more of an art rather than a science as the fabrication lacks some scientific basis. A good model of the stripping operation will shed some light on the scientific principles for different process configurations(simple, vacuum and multi-pressure strippers), evaluate packing performance by determining the optimum height and type of packing for the CO_2

stripping operation and after optimization and sensitivity analysis provide use with some knowledge for addressing scale-up issues.

Desorption occurs by three mechanisms in the stripper. These are: (a) flashing at the stripper feed; (b) normal mass transfer in the stripper; and (c) boiling in the reboiler.

The focus of the present effort is to model the mass transfer that occurs on the packing. The liquid feed is assumed to enter the stripper at the bubble point and as such is being ignored in the current analysis and modelling. The energy requirement for stripping (Q_r) consists of the heat of desorption of CO_2, the heat required to generate steam and the sensible heat required to raise the liquid feed (rich loading) to the temperature of the column.

$$Q_r = Q_{des,CO_2} + Q_{steam\ generation} + Q_{sensible\ heat}$$
$$= -n_{CO_2}\ \Delta H_{abs,CO_2} + n_{H_2O}\ \Delta H_{vap,H_2O} + L\ C_{psolvent}(T_b - T_t)$$

where

n_{CO2} = number of moles of carbon dioxide (mol)

$\Delta H_{abs,CO2}$ = heat of absorption of CO_2 (J/mol)

n_{H2O} = number of moles of water (mol)

$\Delta H_{vap,H2O}$ = heat of vaporisation of water (J/mol)

L = Liquid feed(rich loading) rate (mol/s)

$C_{psolvent}$ = specific heat capacity of the rich solvent (W/mol-K)

T_b = temperature at the bottom of the column (K)

T_t = temperature of the liquid feed (rich loading) (K)

Simple or conventional strippers operating at a pressure of 1.6 atm use steam at 130°C and 2.5 atm. The temperature at the bottom of the stripper is about 120°C. The heat duty for CO_2 stripping decreases at higher pressures. The ratio of the partial pressures of CO_2 and H_2O is a function of temperature. The reactions are very fast and they approach the instantaneous regime. However at higher pressures the steam pressure must be greater.

Vacuum strippers operate at a pressure of about 0.2 atm and make use of low quality steam at a temperature of 70°C and pressure of 0.3 atm. The temperature at the bottom of the stripper is 65°C. The advantage of using vacuum stripping is that lower temperature steam is used and hence more work can be extracted from the turbines in the power plant. The disadvantages include more capital and operating cost due to the installation of compressors and reduced rates of mass transfer. The reactions in this configuration are in the fast reaction regime.

Model Structure

Modeling Assumptions

a) The segments, sections heights into which the packing height is divided, are perfectly mixed.
b) The rich solution is at its bubble point temperature.
c) The condenser and reboiler are treated as equilibrium stages.
d) The desorption of CO_2 is accompanied by a fast equilibrium chemical reaction.
e) The gas and liquid temperatures vary along the column.

Column Specifications

The column specifications are the height of packing to be used, the diameter of the column, and the nominal diameter of the packing. Initially, the reboiler duty is specified but will be varied later.

Operating Variables

The operating variables for the stripper are the rich feed rate, composition and temperature, the steam rate and the operating pressure of the stripper

Equations to be Solved

Since we are using the rate based approach in the stripper, the equations to be solved are:
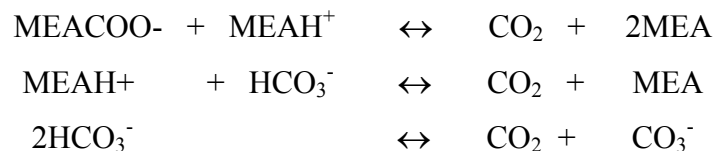
- Material balance
- Equilibrium relations (VLE)
- Summation equations
- Energy balance
- Mass and heat transfer rates

We are also accounting for the fluid mechanics by including equations and correlations to determine or estimate

- The wetted area of the packing
- The liquid and gas phase mass transfer coefficients.

Finally, we have to account for chemical equilibrium in the bulk of the liquid phase.

Reactions Occurring in the Stripper

$$MEACOO- \; + \; MEAH^{+} \quad \leftrightarrow \quad CO_2 \; + \quad 2MEA$$

$$MEAH+ \quad + \; HCO_3^{-} \quad \leftrightarrow \quad CO_2 \; + \quad MEA$$

$$2HCO_3^{-} \qquad\qquad \leftrightarrow \quad CO_2 \; + \quad CO_3^{-}$$

The above equations involve 6 species and three equations. This also illustrates that in addition to the material balance the chemical equilibrium has to be accounted for and this increases the complexity of the problem.

Results and Discussion

Representation of Equilibrium Data

The vapor-liquid equilibrium is represented as the partial pressure of CO_2 in equilibrium with the bulk phase liquid compositions ($P_{CO2}*_{,b}$). Initially, a ten-parameter polynomial fit using Freguia's parameters in Aspen Plus was generated from running simulations over 0.2 – 0.7 mol CO_2/ mol MEA and 60 to 130°C. Figure 1 shows the CO_2 solubility data and fit obtained for 30 wt% MEA. Later on this will be called as a subroutine from Aspen Plus.
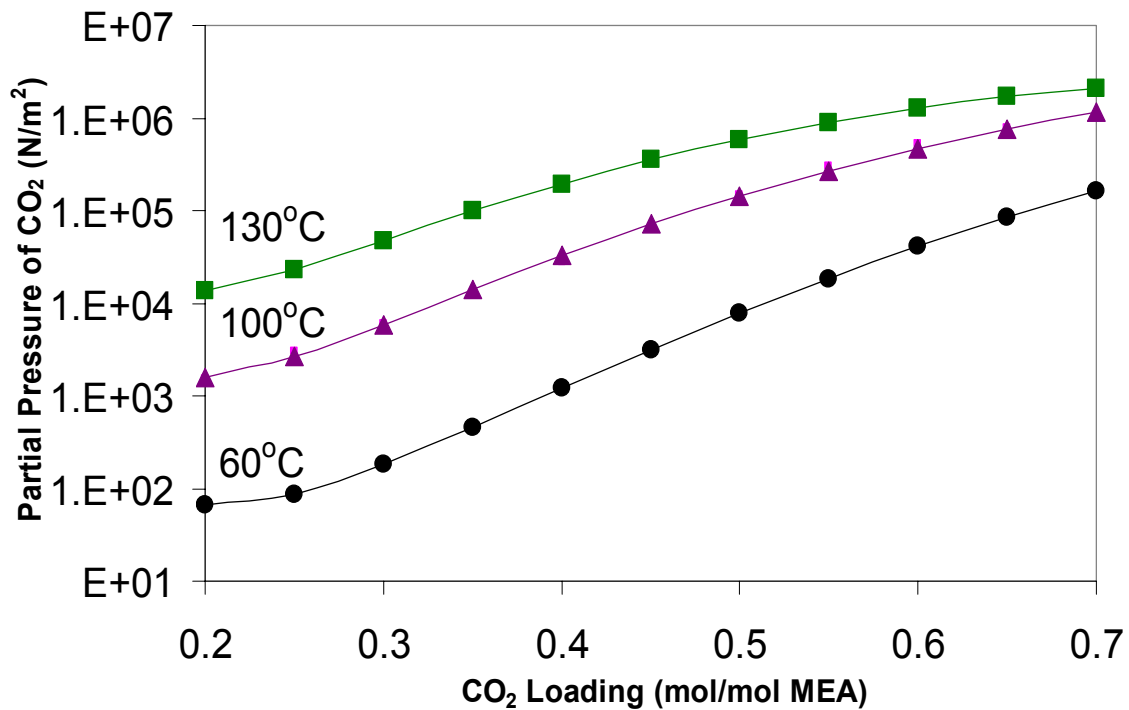

Figure 8. CO_2 Solubility in 30 wt% MEA

The data was fitted to the expression

$$\ln P = a + \frac{b}{T} + c(\ln ldg) + \frac{d}{T^2} + e\frac{\ln ldg}{T} + f(\ln ldg)^2 + \frac{g}{T^3}$$
$$+ h\frac{\ln ldg}{T^2} + i\frac{(\ln ldg)^2}{T} + j(\ln ldg)^3 \tag{5}$$

where T = temperature in K and ldg = loading

a = -138.8

b = 1.476 E+5

c = -88.92

d = -4.615 E+7

e = -23.35

f = 5.023 E+4

g = 4.677 E+9

h = -6.089 E+6

i = 6401

j = -2.701

Representation of Rate Data

The reaction rate will be expressed in terms of normalized flux.

$$k_g^{'} = \text{normalized flux} = \frac{N_{CO_2}}{\left(P_{CO_2^*,b} - P_{CO_2,i}\right)} = f(T, \text{loading}) \tag{6}$$

Initially, $k_g^{'}$ will be extracted from experimental data and approximate models and later from the Bishnoi (2000) and Cullinane (2003) models. Figure 9 shows the normalized flux data for 30 wt% MEA obtained at 60°C by Dang (2001). The approximate boundary layer models follow in the next section.

The Interface Pseudo First Order (IPFO) Approximation

Using this approximation the flux of CO_2 is given by

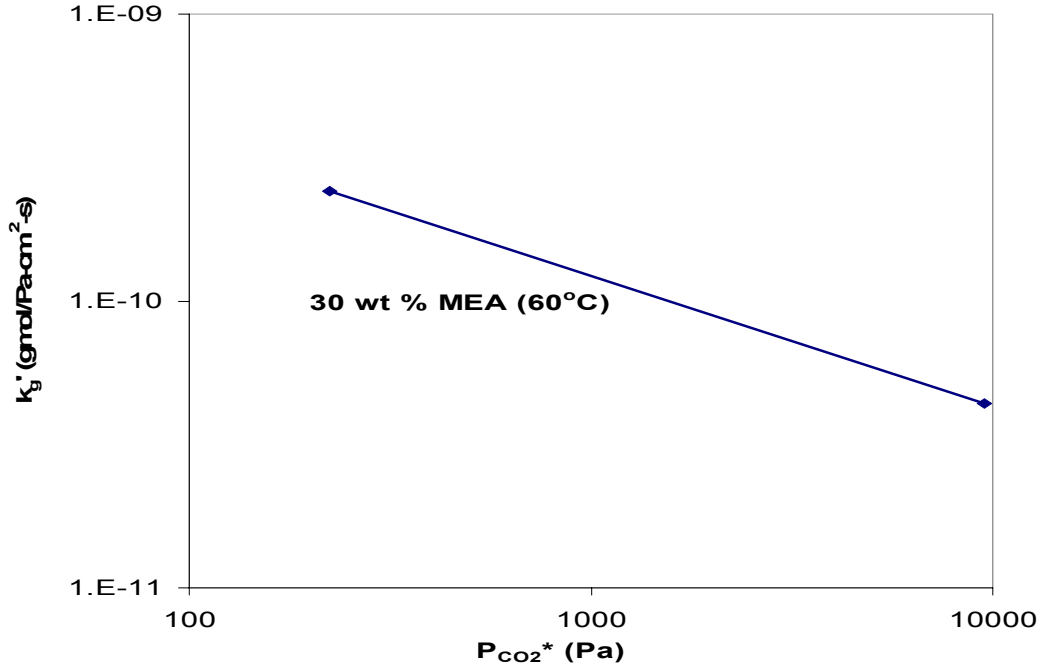$$N_{CO_2} = \sqrt{k_{2,MEA}[MEA]_i \, D_{CO_2}} \quad \frac{P_{CO_2,i} - P_{CO_2^*,i}}{H} \tag{7}$$

Figure 9. Normalized Flux Data for 30 wt% MEA at 60°C (Dang, 2001)

$$P_{CO_2^*,i} = K \frac{[MEACOO-]_i [MEAH+]_i}{[MEA]_i} \tag{8}$$

$$N_{CO2} = k_{1,products} \left([MEACOO-]_b - [MEACOO-]_i^* \right) \tag{9}$$

$$N_{CO2} = k_{1,products} \left([MEAH+]_b - [MEAH+]_i^* \right) \tag{10}$$

$$N_{CO2} = k_{1,products} \left([MEA]_b - [MEA]_i^* \right) \tag{11}$$

The Instantaneous Reaction Approximation

If equations (9) to (11) are solved simultaneously, we arrive at (12) which is what happens when the reaction occurs instantaneously.

$$N_{CO2} = k_{1,products} \left([CO_2]_{T,b} - [CO_2]_{T,i}^* \right)$$

$$= k_{1,products} \frac{\Delta [CO_2]^*}{\Delta P_{CO_2}} \left(P_{CO_2}^*{}_{,b} - P_{CO_2,i} \right) \tag{12}$$

$$= k_g' \left(P_{CO_2}^*{}_{,b} - P_{CO_2,i} \right)$$

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Conclusions and Future Work

In this quarter, the model was refined with a view of accounting for various process configurations and some simulations were run to generate some representation for the equilibrium data for the model. In the next quarter a correlation for the normalized flux will be developed and an equilibrium model for the PZ/K_2CO_3 system will be formulated in time for the first campaign of the pilot plant operations.

Task 2 – Pilot Plant Testing

Subtask 2.1 – Pilot Plant Test Plan

by Eric Chen
(Supported by this contract and by EPA Star Fellowship)

A draft test plan has been developed for the first campaign and will be submitted for approval on December 1. Testing and troubleshooting will have been done on the stripper and absorber (but not the integrated system) prior to the start-up of Campaign 1 due to other work that will be performed with other contracts. The first week of campaign 1 will be to troubleshoot the entire absorber/stripper system with air and water. The focus will be to exercise the combined system and to determine the minimum and maximum operating ranges for each piece of equipment. The second week of the campaign will be to continue troubleshooting, but the plant will be operated with a low concentration of potassium carbonate promoted by piperazine (PCPP) solvent and with 3% carbon dioxide in air. In week three, experiments will first be conducted using the low concentration PCPP solvent and then increased to 5 m potassium/2.5 m piperazine. Runs will be made with 3% CO_2 and the gas and liquid rates will be varied. In order to avoid pinching and maintain a lean feed solution, the stripper will be operated at the maximum steam rate. The final week of the campaign will be to repeat the same experiments of week 3, but with 12% CO_2. In the final two days of the last week, we will attempt to push the solubility limits of solvent in order to obtain better performance.

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

by Eric Chen
(Supported by this contract and by EPA Star Fellowship)

Introduction – Project Management

In this quarter, the bi-monthly meetings were continued to ensure that tasks were completed according the project schedule. The welding bid was delayed by subcontracting issues. The University Physical Plant has completed construction of all three skids. Carbon steel pipe removal was commenced in the month of July and will continue on an as needed basis. Welding began the 22nd of September. An updated Gantt chart shows the revised schedule (Figure 10). We expect the welding to be completed mid-December and we will begin pressure and flow checks and process instrumentation troubleshooting in January. The revised start-up date for the pilot plant is now slated for the beginning of February. However, the commencement of Campaign 1 will be contingent on the initial operational difficulties encountered during the troubleshooting phase of plant start-up.

Experimental – Equipment Modifications

Welding Bid

The bids were re-advertised in August due to the unexpectedly high bids. Lanco Welding and Fence was selected as the winner of the welding bid contract. The total cost for the completion of the welding contract is $37,000 and will be completed over an 11 week period. The Lanco outfit consists of a welder and a pipe fitter working together. All work will be supervised by one of the SRP personnel. The welding work is scheduled to be completed by the second week of December, with a one week contingency.

The welders have completed construction of the 6-inch vapor line running from the top of the stripper to the condenser (DWG 6100-605). Table 7 gives the current status on the progress of the welding job. Line P2013 has been visually inspected and hydro tested and has received final approval. The welders have begun work on the cooling water lines for the solvent cooler (DWG 6100-609) and have completed approximately 10% of the work.

Heat Exchangers/Support Racks

The three support racks for the heat exchangers and process instrumentation have been completed. All three support structures have also been placed at their respective future locations. However only the filter skid has been installed and bolted to the ground floor and wall. The other two skids still need to be shimmed to the proper level and permanently bolted to the ground floor. The two solvent heaters, solvent cooler, and the associated flowmeters and valve have been permanently mounted to each of their respective support racks.
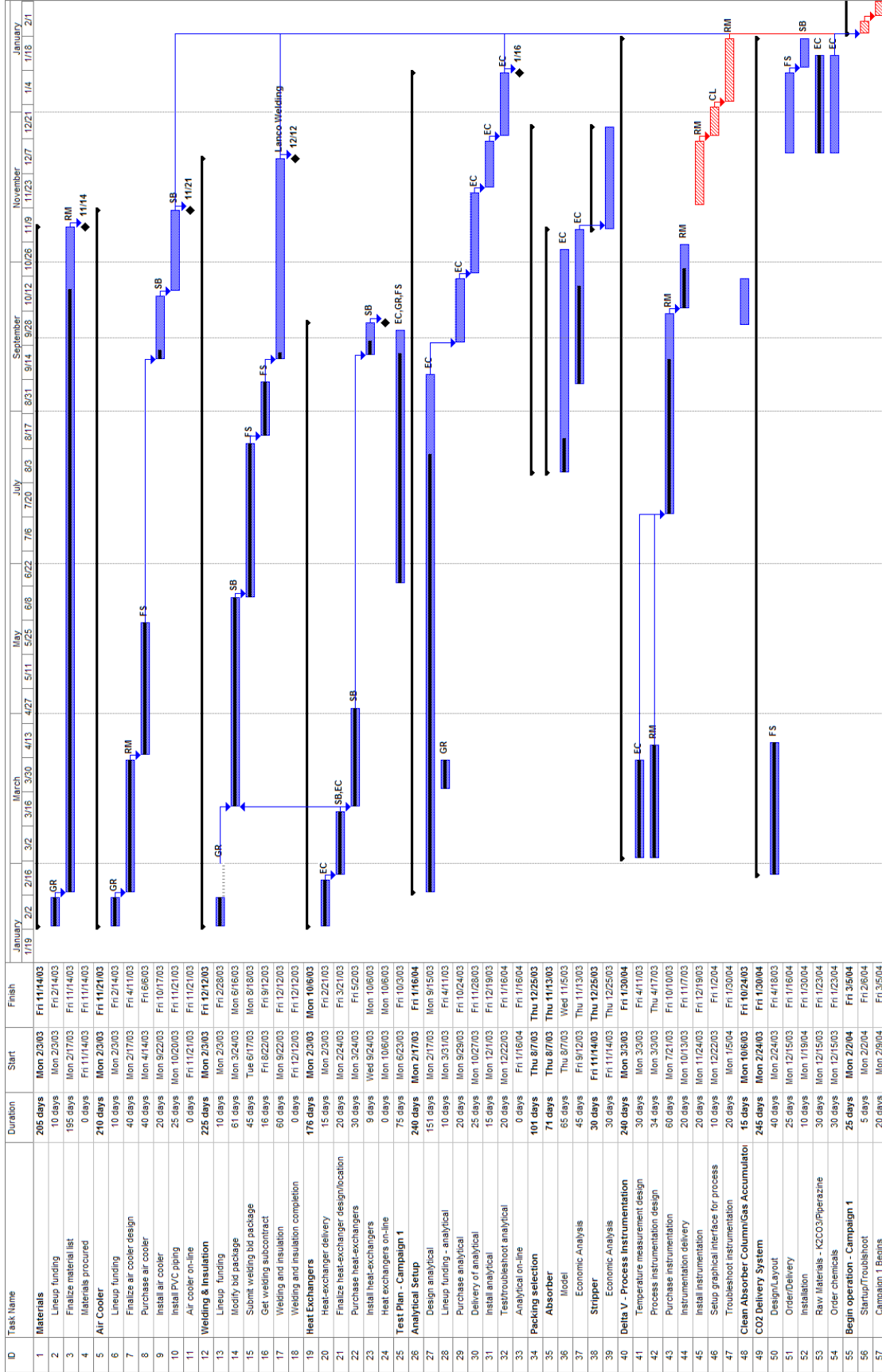
Figure 10. Gantt Chart for CO₂ Removal Project

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Table 7. Welding Job Progress

Drawing No.	Line	Fabrication (%)				Initial/Visual	Hydro Test	Final
		25	50	75	100	Inspection		Approval
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 procured. The air cooler will now be installed directly downstream of the absorber gas outlet instead of downstream of the blower. Due to the heavy weight of the air cooler, management decided that it would be safer to support the air cooler from the bottom rather than suspending it. The air cooler will be mounted on the 4th level platform. Since the air cooler will be removing entrained solvent, it was decided that a mist eliminator would not be needed. We have contacted a UT structural engineer to aid with the design of the air cooler support structure and are awaiting his response.

Process Instrumentation

The Micro Motion® flowmeters have been mounted on the support structures along with the associated process piping. The temperature measurements for the absorber will be conducted using RTD's. We are in the process of negotiating with Emerson Process for a discount on the RTD probes and transmitters and are attempting to get additional cost-sharing funding from CD Tech.

Results and Discussion (Equipment List)

Table 8. New Equipment Status lists the current status for each of the new pieces of equipment. Before the air cooler can be installed, the support structure must be designed and constructed. The design is currently being reviewed by a UT structural engineer.

Table 8. New Equipment Status

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

Conclusions and Future Work

The contracted welding work will be completed by mid-December. The air cooler support structure will need to be designed and fabricated prior to the installation of the air cooler. The RTD's will need to be purchased and all of the process instrumentation will need to be installed, wired and tested. The Delta V process interface for the absorber/stripper system will also need to be setup. The analytical methods will be further refined and the methods exported to the instruments out at the Pickle Research Center. The absorber model and economic analysis of packing materials for the absorber/stripper columns will also need to be finished.

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