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. Progress has been made in this reporting period on three subtasks. The rigorous Electrolyte Non-Random Two-Liquid (electrolyte-NRTL) model has been regressed to represent CO₂ solubility in potassium carbonate/bicarbonate solutions. An analytical method for piperazine has been developed using a gas chromatograph. Funding has been obtained and equipment has been donated to provide for modifications of the existing pilot plant system with stainless steel materials.

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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 have made contributions this quarter to the scope of this project. Three new graduate students have been recruited to start work with DOE support in January 2003 for direct effort on the scope of this contract.

Progress has been made on three subtasks in this quarter:

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

Work has been initiated on a rigorous Electrolyte Non-Random Two-Liquid (electrolyte-NRTL) model to simulate the thermodynamic data for promotion by piperazine. This initial model uses a stand-alone FORTRAN code. As a continuation of work funded by the Texas Advanced Technology Program, the rigorous electrolyte-NRTL model has been regressed to represent CO₂ solubility in potassium carbonate/bicarbonate solutions.

Subtask 2.1 – Pilot Plant Test Plan

An analytical method for piperazine has been developed using a gas chromatograph. It has been tested in experiments to measure oxidative degradation of piperazine.

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

The process and instrument diagram (PID) and process flow diagram (PFD) have been reviewed by DOE and other industrial sponsors. DOE has approved additional budget to permit modifications to the pilot plant to include stainless steel equipment. Huntsman Chemical has also agreed to donate relatively new stainless steel heat exchangers and columns for use in this program.

Future Work

We expect the following accomplishments in the next quarter:

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

The stand-alone FORTRAN model will be applied by Tim Cullinane to thermodynamic data for CO₂/water/potassium carbonate/piperazine. Work will be initiated by a new student (Marcus Hilliard) with the electrolyte-NRTL model in AspenPlus.

Subtask 1.3 – Develop Integrated Absorber/Stripper Model

Eric Chen (a new student to this project) will develop a simple integrated absorber model in EXCEL. Babatunde Oyenekan (a new student) will initiate development of an integrated stripper model.

Subtask 2.1 – Pilot Plant Test Plan

Terraun Jones will complete development of analytical methods for piperazine and potassium using gas chromatography and ion chromatography. Eric Chen will develop a preliminary pilot plant test plan.

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

The equipment donated by Huntsman will be installed. Purchasing of other equipment and materials for the pilot plant will be initiated. The column packing and internals will be selected.

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

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

by J. Tim Cullinane

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

The work presented here is a continuation of the development of aqueous potassium carbonate/piperazine mixtures for CO₂ removal from flue gas. Previously, data on CO₂ partial pressure, piperazine speciation, and CO₂ absorption rates was collected (Cullinane, 2002). A rigorous thermodynamic model is now being developed to predict the equilibrium and speciation in potassium carbonate/piperazine mixtures for future use in process and kinetic modeling. The model, taken from previous work by Austgen (1989) and Posey (1996), utilizes the electrolyte-NRTL model (Chen *et al.*, 1982) to estimate activity coefficients and solve the necessary equilibrium expressions. Methods for further thermodynamic measurements are being developed.

Equilibrium Modeling

Previous work in modeling the potassium carbonate/piperazine mixtures focused on the development of a simple model to describe equilibrium behavior (Cullinane, 2002). While a simple model is capable of approximating the behavior of the system, a more thermodynamically rigorous model is desirable for describing the complex solution characteristics for future use in rate and process models.

The rigorous thermodynamic model selected for the concentrated solutions is the Electrolyte Non-Random Two Liquid model (Electrolyte NRTL) developed by Chen *et al.* (1982). The model uses binary interaction parameters, τ , to represent the impact of a molecule or ion 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 model the excess Gibbs energy. The first, the Pitzer-Debye-Huckel term, is a long-range contribution to describe ion-ion interactions at low concentrations. The second term, the Born correction, accounts for changes in the dielectric constant of the solution as the solvent reference state changes. Finally, short-range contributions that are dominant at high concentrations are represented by the NRTL model (Renon and Prausnitz, 1968). The excess Gibbs energy of the three terms can be added to arrive at a total excess Gibbs energy for each term.

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

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

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

In the model used in this work, all molecule-molecule and ion pair-ion pair parameters are set to zero. Also, all τ 's are assumed to have no temperature dependence unless otherwise specified. Henry's constant of CO₂ is assumed to be that of CO₂ in water. Equilibrium constants used are those found in Posey (1996). A more thorough discussion of electrolyte NRTL theory as it pertains to gas treating solvents can be found in Austgen (1989) and Posey (1996).

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

The regression of parameters is accomplished using a non-linear regression package called GREG (Caracotsios, 1986). Experimental, or measured, values are compared to values predicted by the model. In an iterative process, user defined parameters are adjusted until the least squares difference of these values is minimized.

Currently, model parameters have been adjusted to fit data for the activity of water in K₂CO₃-water mixtures as published by Aseyev (1999). This data includes freezing point depression, boiling point elevation, and vapor pressure measurements giving a wide range of both temperature and concentration. The data varied in temperature from 235 to 393 K and 0.0 to 50 wt% K₂CO₃. Four adjustable parameters were used to fit the data set: water-ion pair, its temperature dependence, ion pair-water, and its temperature dependence. The form used for temperature dependence is

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

The values of the four regressed parameters as well as their standard deviations are shown in Table 1 and are consistent with other salt solutions as found by Chen *et al.* (1982). With the regressed parameters, the model predicts the activity coefficient of water within 2% of the values given in the literature. The values of these parameters will be fixed at the regressed values throughout the remainder of this work to maintain a thermodynamically consistent model.

Parameters describing KHCO₃ behavior were regressed using VLE data as reported by Tosh *et al.* (1959) and freezing point depression data reported by Aseyev (1999). The values of the regressed parameters are also reported in Table 1. A normalized parity plot of the predicted CO₂ partial pressures is shown in Figure 5. The figure shows a large degree of scatter among the data points. Within the spread, it appears that predictions of 20 wt% K₂CO₃ are centered lower than experimental values, predictions of 30 wt% K₂CO₃ agree with experimental data, and predictions of 40 wt% K₂CO₃ 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%.

Data on speciation of loaded piperazine solutions (Bishnoi, 2000) and potassium carbonate/piperazine mixtures (Cullinane, 2002) will be used to regress the τ 's necessary

to describe the piperazine contribution to activity. Data on piperazine volatility, water activity, and CO₂ vapor pressure of these solutions will be gathered to further support the modeling.

Table 1. Regressed Parameters for Potassium Carbonate-Potassium Bicarbonate/Water Interaction Parameters

		A	Std. Dev. of A	B	Std. Dev. of B
1	H ₂ O,K ⁺ ,CO ₃ ²⁻	8.652	0.162	860.9	371.1
2	K ⁺ ,CO ₃ ²⁻ ,H ₂ O	-4.304	0.033	-215.9	74.6
3	H ₂ O,K ⁺ ,HCO ₃ ⁻	6.722	0.039	1614.2	153.4
4	K ⁺ ,HCO ₃ ⁻ ,H ₂ O	-3.001	Indet.*	-122.0	Indet.*

* Indeterminate: Represents a high correlation between 3 and 4.

Figure 5. Electrolyte-NRTL Model Predictions of CO₂ Vapor Pressure in Aqueous Potassium Carbonate Solutions (Tosh *et al.*, 1959) Using Parameters Shown in Table 1

Thermodynamic Measurements

An apparatus, as depicted in Figure 6, is being developed to measure the volatility of piperazine and water in loaded and unloaded potassium carbonate/piperazine mixtures. Nitrogen and carbon dioxide flowrates are controlled and mixed to maintain the desired CO₂ partial pressure and a total flowrate of 2 to 5 L/min. The gas bubbles through a pre-saturator to improve temperature control and ensure 100% saturation from the equipment. The pre-saturator is a modified calorimetric bomb filled with water and submerged in a heat bath for temperature control. The gas is sent to a gas impinger where a majority of the gas-liquid contact is allowed. The impinger has been modified to incorporate a

temperature control system. A type-T thermocouple is used to measure the temperature of the vapor space inside the impinger. A temperature controller in conjunction with a heating jacket maintains the temperature at the desired setpoint. The sparged gas travels upwards 7 to 10 inches through the solution and into a vapor region to reduce entrainment. Glass wool has also been inserted approximately 2 inches above the liquid level to reduce entrainment. The saturated gas is then sent through a heated line to an FT-IR spectrometer for analysis. The FT-IR is capable of continuous, multi-component analysis enabling piperazine, water, and CO₂ vapor concentrations to be measured.

Figure 6. Apparatus for the Determination of Piperazine Volatility

The apparatus has been tested at various temperatures, gas flowrates, and liquid levels using pure water and a comparison to a published vapor pressure curve for water (Figure 7). The apparatus accurately measures the vapor pressure between 40 and 70°C. At the high gas flowrates, the heat input is insufficient to maintain temperatures higher than 70°C. More tests and modifications are needed to increase the viable temperature range of the equipment.

Figure 7. Water Vapor Pressure from Dean (1992) (Lines) and Measured Values from This Work (Points)

In addition to testing the apparatus for accuracy, the FT-IR spectrometer was calibrated for piperazine vapor measurements. A known amount of piperazine, approximately 2 g, was placed in a test tube and then placed in a sample cell. A sample cell was created using a calorimetric bomb; the bomb was submerged in a heating bath to maintain a constant temperature as measured by a thermistor. A stream of nitrogen at a constant flowrate entered the sample cell, sweeping piperazine vapor into the FT-IR spectrometer. After approximately 5 hours, the piperazine was removed and the lost mass was determined. With the known flowrate, weight loss, and elapsed time, a piperazine concentration was calculated and matched with the corresponding spectrum created by the FT-IR spectrometer.

Three measurements were made (68.9, 85.2, and 100.6°C) giving three vapor concentrations (12.3, 41.4, and 128.9 ppm_v). In Figure 8, the concentrations are plotted versus the peak intensity seen on corresponding spectrum. A trendline, with the y-intercept set to zero, is also shown. Note the linear behavior indicating that Beer's law is followed in this range and accurate measurements were made. The three spectra were added to the FT-IR reference library and will be used for analysis of piperazine vapor pressures.

Figure 8. Calibration of Piperazine Concentration for the FT-IR Spectrometer

Task 2 – Pilot Plant Testing

Subtask 2.1 – Pilot Plant Test Plan

by Terraun Jones

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

Summary

Analytical methods have been developed for solutions of potassium carbonate containing piperazine. These methods have been tested in experiments to measure the degradation of piperazine. 3.6 Molal KHCO_3 /1.8 Molal Piperazine was degraded at 40°C and 60°C for several days. Samples were taken every 24 hours and analyzed using gas chromatography. Diethanolamine is a major degradation product with a rate of appearance of 5.7mM/hr at 40°C and 1.9 mM/hr at 60°C. Piperazine loss rate at 40°C is 3.2 mM/hr, and at 60°C it is 1.3 mM/hr over the course of the experiment. Extra components were detected but are not identified or quantified.

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 gas and ion chromatography methods devised for alkanolamines, piperazine, potassium carbonate, metals, and acid anions and products that result from oxidative degradation of the solutes, and will present preliminary findings for piperazine degradation in promoted potassium carbonate solutions.

Gas Chromatography

Method Setup

The gas chromatograph (GC) is an HP 5890 with an HP 7673 Autoinjector. The column is an HP-5 capillary column that is 30 meters and has a .53mm and 1.5μm lining. The system is a split/splitless injector with helium as the carrier gas. The split ratio is the ratio of column gas rate to overall gas rate, which is 20, with column gas rate of 10ml/min. All of this is checked with a bubble flowmeter. The rest of the gas is vented. The split is designed to lessen the work load on the column for separations by diluting the vaporized solution. Air, hydrogen, and a makeup gas of helium are used for flame ionization detection (FID) for better peak detection. The air rate is 400ml/min. The hydrogen rate is 30ml/min and the makeup gas rate is 10ml/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. The run time is 12 minutes. The first three minutes run isothermally at 40°C. The temperature is then ramped up to 140°C at 20°C/min. The column runs at 140°C for four minutes to push out heavier components. The injector and detector are set at 180°C so we do not achieve thermal degradation of the components. The system is computer automated with Galaxie Chromatogram software, which fully controls the injection and detection process.

Results

Figure 5 shows a sample solution of MEA, piperazine, diethanolamine (DEA), ethylenediamine (EDA) and water with roughly equal mass analyzed by GC. The first peak at 1.3 minutes is ethanol, which is used for internal standard calibration. The EDA comes out first with the top of the peak coming out at 3.1 minutes. MEA immediately comes out after with the peak coming at around 3.5 minutes. Piperazine came out at 6.4 minutes and DEA came out at 9.1 minutes. EDA and MEA, which have similar molecular weights (60.10 and 61.71 grams/mole, respectively) were separated well, even at 20wt% of each. The ramping sharpens up the piperazine (MW 86.13 grams/mole) peak. DEA (MW 105.1 grams/mole) has a high boiling point (roughly 260°C) which ventures into the thermal degradation regime of the lighter components. Its peak is not as sharp because of this. Water is not detected in the FID and therefore has no peak.

Figure 5: Gas Chromatogram for Calibration with 1.4wt% of Each Amine

Using this method, the components were calibrated. Figures 6 and 7 show calibration curves for piperazine and DEA, respectively. The starting solution was diluted with water and a water/ethanol mixture to get varying wt% concentration of the amines. Piperazine, EDA, MEA and DEA were all calibrated from roughly 1 wt% to roughly 17 wt% of each. The external and internal calibrations are included. They all exhibit good linearity over the range of weight percents. Because of these results, the GC was used to analyze the solutions with confidence.

Figure 6: Calibration Curve for Piperazine Using Standard Amine Solution of 20wt% Amines and Multiple Dilutions with Water

Figure 7: Calibration Curve for DEA with Same Conditions as Piperazine

Piperazine Degradation

Experimental Setup

Air at 1L/min is mixed with CO₂ gas at 20 cc/min to make a 2% CO₂ stream. This stream is saturated at reactor temperature in a 3L water bath. The saturated air stream is sent to the reactor. The reactor is glass, jacketed, and connected to a temperature bath to regulate the temperature. Syringe samples are taken once a day at approximately 24-hour intervals over 7 days. The solutions are analyzed by GC or IC for content. The volume and mass of the sample is recorded as well as the time and the volume in the reactor. The volume of the reactor is recorded by measuring the height of the solution. This determines whether too much or not enough water is getting into the system.

Results

Figure 8: GC for 3.6m KHCO₃/1.8m PZ Degraded at 40°C after 48 Hours

Using GC, degraded piperazine solutions were analyzed. These solutions contain potassium bicarbonate at high concentration and iron at low concentration. These solutions are diluted to prevent clogging due to salt collection. After the weight percents are found, the concentration is 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. It is assumed that since the samples are diluted and rapidly heated, all carbamates are returned to the original amines. A sample chromatogram from 3.6m KHCO₃/1.8m Piperazine with 1mM Iron (II) shows DEA and Piperazine after 48 hours. None of the other investigated alkanolamines were detected.

Figure 9: Piperazine Loss for 3.6m KHCO_3 /1.8m Piperazine with 1mM Fe^{++} in 1 L/min Air with 2% CO_2

Figure 10: DEA Production for 3.6m KHCO_3 /1.8m Piperazine with 1mM Fe^{++} in 1 L/min Air with 2% CO_2

Piperazine and DEA were plotted for two experiments. The experiments are the same concentration but at 40°C and 60°C. The rate of Piperazine loss at 40°C is 3.2 mM/hr, and at 60°C is 1.3 mM/hr over the course of the experiment. The maximum rate of DEA production is 5.7mM/hr at 40°C and 1.9 mM/hr at 60°C. DEA appears to peak out for each at 48 hours. It also appears more piperazine is lost and DEA is produced at 40°C. This may have a lot to do with the mass transfer properties of oxygen in these solutions, which is mainly responsible for oxidative degradation. DEA also shows a gradual decline as well, showing that it is being degraded. There are also 2 extra peaks of the same magnitude as the DEA peaks. At present, they have not been identified, but initial estimation of the concentrations is between 10 and 15 mM. These estimates were made based on GC separation properties and FID detector properties. These peaks probably have molecular weights within the range of 70 to 75 grams per mole.

Conclusions and Recommendations

Industrially, both GC and IC have been used to analyze alkanolamine solutions. For the GC methods, the amines themselves can be separated with good linearity over the desired ranges of wt% for the solutions of interest. However, any metals and anions are collected in the injector. For a large number of samples with high salt contents, such as potassium carbonate solutions, injector clogging becomes an issue. Diluting the solutions can help with lots of sample injections. The IC method can be used for the ionic species and salting is not an issue. However, components in large quantity, such as MEA in MEA solutions, and potassium in potassium carbonate solutions, can overpower other components in small quantities, such as metals characteristic of corrosion, and their concentrations cannot be detected. Diluting to low levels and adding the less concentrated components so the analytes are of the same detectable range can help with this. Peak trailing in the amines was reduced with a faster eluant flow in both GC and IC, but the faster flows can result in merging of peaks, which destroys good chromatography. The methods described above represent a good compromise of all chromatography complications and give reliable results.

Initial degradation experiments show a loss of piperazine being roughly the same as other commonly used alkanolamines for acid gas scrubbing. DEA appears to be a chief amine degradation product in solution. Other products appear with roughly the same concentration as DEA but have not been identified. Because DEA is produced, ammonia may also be produced.

Future Work

Piperazine degradation will be further studied. The extra components from the degradation will be identified. The gas coming off the reactor will be analyzed for ammonia and other small amines. Solutions of differing piperazine and potassium carbonate concentrations will be degraded as well as piperazine only for comparison. Temperatures seen in acid gas scrubbers will be used. Metals such as iron, usually resulting from the corrosion of carbon steel, and vanadium, a commonly used corrosion inhibitor in potassium carbonate solutions, will be studied to understand their effects on oxidative degradation.

Subtask 2.2 Design, Modifications, Order Equipment and Packing Materials by Frank Seibert

A process and instrument diagram (PID) and process flow (PFD) have been developed. They have been reviewed by Dr. Ram Srivastava (representing DOE) and by representatives of Professor Rochelle's Acid Gas Consortium. The proposed PID appears to be well designed with the only concern that there may not be enough surge capacity for the recycle air to the absorber. We are currently reviewing different alternatives to provide such capacity.

We are currently evaluating potential contacting internals to be tested. One industrial representative of the Separations Research Program has suggested that we study light-weight, low-liquid hold-up internals such as packings. Since these columns are expected to have very large diameters (up to 40 ft), the cost of supporting heavy internals is significant. The person also expressed concern regarding liquid distribution.

Typical metal pan and trough-type distributors are very heavy and will require significant beam support. Further, for such large diameter columns it is difficult to make them level enough to handle the relatively low liquid flow rates we require.

We recently completed an exploratory study of another type of liquid distributor that is light in weight and low in hold-up: the Fractal distributor. The study was jointly funded by a DOE Grant to Amalgamated Research Inc. (Twin Falls, Idaho) and by the Separations Research Program (UT Austin). The purpose of our study was to compare two Fractal distributor designs (10 distribution points/ft² and 40 distribution points/ft²) with two conventional liquid distributors, orifice (40 distribution points/ft²) and a trough drip tube (13.5 distribution points/ft²).

The effective mass transfer area (a_e) of a light-weight, high surface area structured packing (Montz B1-500) was determined using the air/carbon dioxide/caustic system. The technique has been described by Professor Rochelle and his graduate student, Ian Wilson. As shown in Figure 11, the Fractal distributors provided the highest utilization of the available packing area. The encouraging efficiencies of the exploratory study may result in a reliable, cost-effective alternative for liquid distribution in large diameter packed columns. We have not measured the relative pressure drops of the distributors. Further studies with the Fractal distributor are recommended.

For the large diameter column and the need for low pressure drop, spray distributors should also be investigated. The concerns with such distributors are (a) entrainment, (b) uniformity of the distribution to the packed bed, i.e., underlap and overlap for patterns from multiple nozzles, and (c) turndown capability. We have studied the entrainment effects and our results are summarized in a paper by C. Trompiz and J.R. Fair (*Ind. Eng. Chem. Research* **39**, 1797-1808, 2000). Our conclusion was that for a nozzle providing a narrow distribution range of large drops, entrainment can be minimized. The results have been applied by co-author C. Trompiz to large-diameter industrial packed columns, and deleterious entrainment has been greatly reduced and distribution patterns have been satisfactory. The potential problem of turndown can be addressed by further studies. In summary, the spray distributor is the ultimate in low pressure drop, and its potential should be investigated.

Future Work (Next Quarter)

Work in the next quarter will focus on the procurement and installation of the stainless steel heat exchangers. In addition to completing the review of the need for possible recycle air surge capacity, our piping isometrics will be finalized. We are also seriously exploring the option of using relatively new stainless exchangers and columns donated by Huntsman Chemical. The donation was officially offered to the Separation Research Program on January 13, 2003.

Figure 11. Comparison of Distributors at an f-factor = 1.29 ft/s (lb/ft³)^{0.5}

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