A "GREENHOUSE GAS" EXPERIMENT FOR THE UNDERGRADUATE LABORATORY

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Lowering CO_2 emissions might directly ease anticipated negative impacts on human and planetary health.[1] It is desirable, then, to introduce greenhouse gas experiments into the unit operations laboratory to enhance students' sense of relevance and broader impact. Acid gas scrubbing with hindered amines is used commercially, but is impractical in the student laboratory. A useful alternative is scrubbing of CO_2 with aqueous NH_3.

There is strong interest in CO_2 removal with NH_3, especially in countries that depend heavily on coal combustion for electricity generation, such as China. Several studies[2-4] have examined the impact of various operating parameters on CO_2 capture efficiency. There are also comparisons of the relative CO_2 removal efficiency of using ammoniated water as compared to amine solutions.[5,6] Even the American Electric Power coal-fired power plant in West Virginia is testing CO_2 capture using chilled ammonia.[7]

Simple ammonia absorption in wetted wall or packed columns is a staple of unit operations student laboratories. A traditional mass transfer coefficient and transfer unit analysis are typical.[8] Modern simulation software provides an opportunity for sensitivity analyses supported by experimental data.[9] An engineering correlation approach that incorporates the various operating parameters that affect the overall column efficiency offers students a design component. Reactive absorption, wherein a chemical reaction or neutralization occurs upon absorption of the gas into the liquid, adds a dimension that challenges the student to potentially integrate reactor engineering and mass transfer.[9] Modification of an existing ammonia absorption experiment for CO_2 capture presents a viable opportunity to enhance the unit operations laboratory.

In this paper, an existing NH_3 absorption student experiment was altered to scrub CO_2 from a simulated flue gas with ammoniated water in a counter-current packed column. Several operating parameters were considered, and a kinetic model for the CO_2 capture is applied. An engineering correlation relating CO_2 capture efficiency is developed.

SCRUBBING REACTIONS

The relevant absorption reactions in this study, as described by Hatch and Pigford,[10] are:

$$NH_{3(aq)} + CO_{2(aq)} \rightarrow NH_2COOH_{(aq)} \quad (I)$$

$$NH_2COOH_{(aq)} + NH_{3(aq)} \rightarrow NH^+_{4(aq)} + NH_2COO^-_{(aq)} \quad (II)$$

Subsequent reactions of the carbamate yield ammonium carbonate [$(NH_4)_2CO_3$] that can be recovered for NH_3 regeneration, and CO_2 can be sequestered. During the absorption, Zeng, *et al*.[2] argued that the liquid phase CO_2 concentration approaches zero due to a relatively fast reaction. So, the

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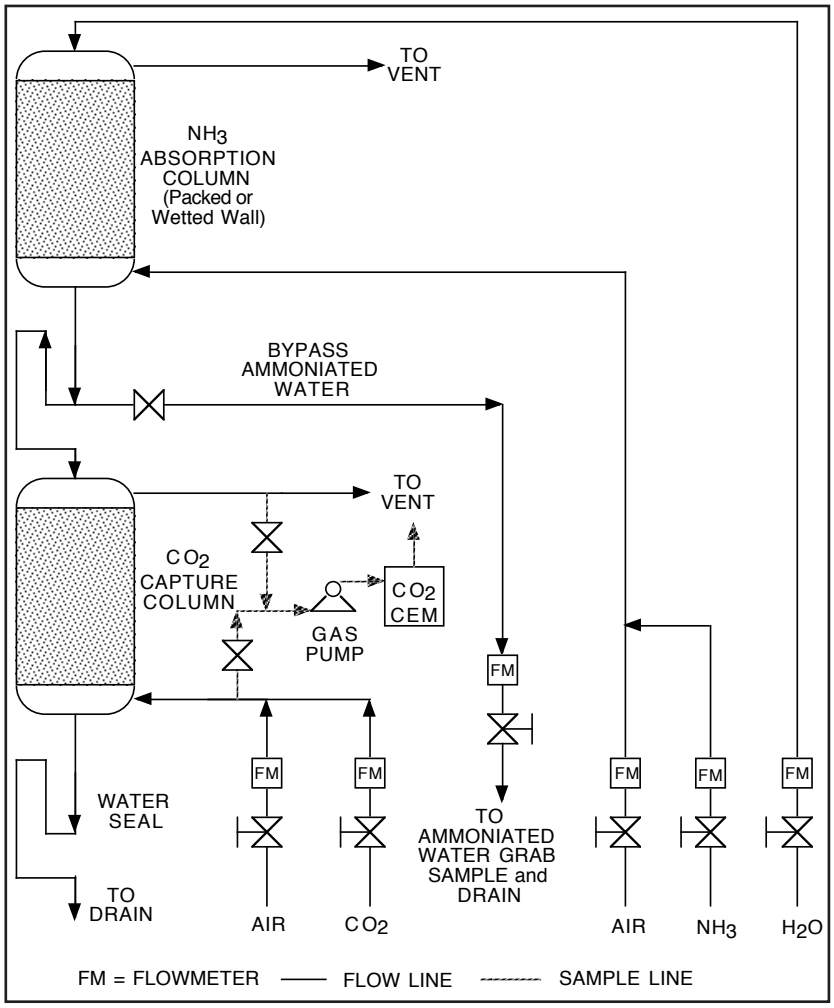

Figure 1. *Schematic of the generic experimental system.*

overall CO_2 removal rate is likely mass transfer controlled.

For the current system of air/CO_2/NH_3/water at one atmosphere, the solubility of CO_2 in water is small compared to the reactive absorption. There is also some small stripping of NH_3 by air from the liquid[11]; this is ignored. The overall depletion of dissolved NH_3 is assumed small. A CO_2 species balance in the gas forms the kinetic model.

KINETIC (RATE-BASED) MODEL FOR MASS TRANSFER

Consider a control volume of differential length Δz from the packed column of diameter D, cross section A. Water containing dissolved NH_3 enters at a total molar flux L at $z + \Delta z$. The air/CO_2 mixture enters countercurrent at z at a total molar flux V. Through the column, V is not constant due to the loss of CO_2 to the liquid phase. The resulting steady state CO_2 differential species balance is:

$$\frac{d(yV)}{dz} = -K_y a_v \left(y - y^*\right) \qquad (1)$$

where y = gas phase CO_2 mole fraction and $K_y a_v$ is a lumped mass transfer coefficient (mole fraction units) times transfer area per unit packing volume. The quantity y* is the gas CO_2 concentration that would be in equilibrium with the liquid of CO_2 mole fraction x at point z, as per Henry's Law ($y^* = K_H x$, K_H=Henry's constant). Using $V' = (1-y)V$, where V´ = molar air flux (constant), and $y^* \rightarrow 0$ due to a fast reaction,[2] Eq. (1) becomes:

$$\frac{dy}{dz} = -\frac{K_y a_v}{V'} y(1-y)^2 \qquad (2)$$

The overall mass transfer coefficient $K_y a_v$ (kmole/hr-m^3-mole fraction) can be converted using $K_y a_v = K_G a_v P$ where P = the total pressure (kPa). Assuming $K_G a_v$ (kmole/hr-m^3-kPa) is roughly a constant for a particular run, Eq. (2) integrates to:

$$St \equiv \frac{K_G a_v Z P}{V'} = \ln\left[\frac{y_o(1-y)}{y(1-y_o)}\right] + \frac{y_o - y}{(1-y)(1-y_o)} \qquad (3)$$

where Z = packing height (m), and V´ = air flux (kmole/hr-m^2). The left hand of Eq. (3) is a mass transfer Stanton number (St)—a ratio of mass transfer rate to bulk fluid rate. If St is too low, there is poor mass transfer. Defining the CO_2 capture on a molar rate basis:

$$CO_2 \text{ capture} = \frac{y_o - y_{exit}}{y_o(1-y_{exit})} \qquad (4)$$

where y_o and y_{exit} = feed and effluent CO_2 mole fractions. Eqs. (3) and (4) suggest a correlation of CO_2 capture efficiency (%) vs. Stanton number (St).

LABORATORY DESCRIPTION

Figure 1 shows a generic schematic of the system used. The original NJIT layout was constructed long ago with three main components: a lower packed column to humidify air, a wetted wall column to absorb ammonia from the humidified air, and finally an upper packed column to scrub any residual ammonia from the air leaving the wetted wall column. In this study, students alternately used the wetted wall and upper packed column as ammoniated water sources as indicated in Figure 1.

Currently, a combined air and CO_2 stream flows upward into the lower packed column (0.1 m ID, 0.79 m length, 0.0127 m ceramic berl saddles). Ammoniated water is made either in

the upper packed column or the wetted wall. The ammoniated water flows into the CO_2 scrubbing column by gravity. Its flow rate is determined by subtracting the metered flow rate of liquid from either source that is rejected to drain from the feed water rate to that source. This rejected flow is required to avoid loading or flooding the CO_2 scrubber.

Samples of ammoniated water are titrated with standardized HCl solution (0.1 M) and methyl red indicator. Inlet and outlet scrubber gas samples are withdrawn through a desiccant tube with a diaphragm pump, and analyzed with an on-line, non-dispersive infrared CO_2 analyzer (X-STREAM™). Calibration (15 mole % CO_2, balance N_2) and zero (N_2) gases are used for routine verification of the analyzer.

All gaseous and liquid flows are measured with calibrated rotameters. Steady-state is judged when the CO_2 concentrations are stable. The system operates at room temperature (~ 23 °C) and 1 atmosphere. Column pressure drops are minimal.

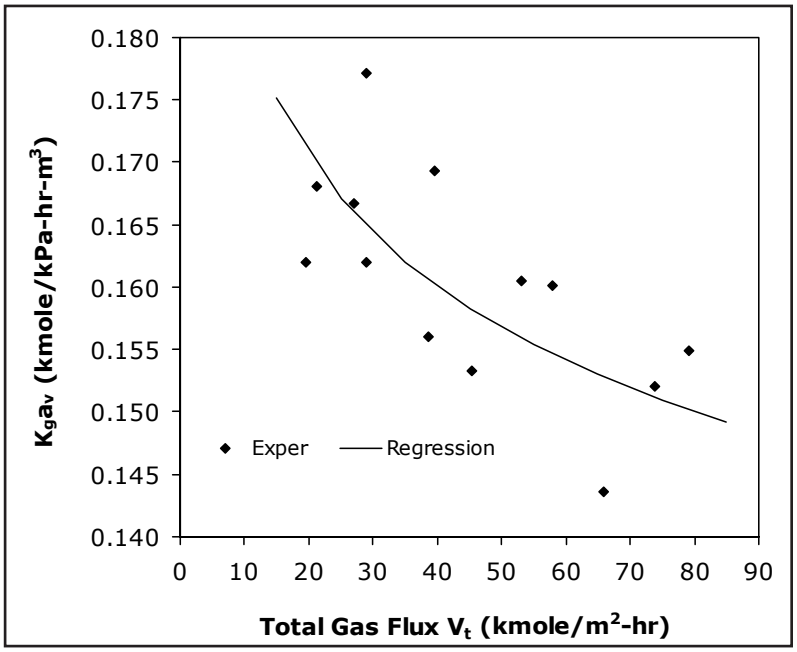

Figure 2. *Dependence of mass transfer coefficient on inlet total gas flux. Operating conditions: C_{NH3} = 0.009 mass fraction, P_{CO2} = 9 kPa, L_v = 13.6 m³/hr-m².*

ALTERING AN EXISTING ABSORPTION EXPERIMENT

How an existing ammonia absorption unit operations experiment is altered for CO_2 reactive absorption depends on available resources. An independent source of ammoniated water is required. This can either be a packed column or wetted wall. If the new CO_2 absorber is to be a wetted wall, then the mass transfer coefficient correlation presented later will not apply, although the general theory will be similar.

It is recommended that, if possible, the ammoniated water source be physically located above the CO_2 scrubber. In this way, the liquid can flow by gravity into the scrubber. If not, a corrosion resistant pump will be required to feed the scrubbing liquid.

Finally, if not available, an infrared CO_2 analyzer represents the major upgrade expense. The 2012 price for the new analyzer used in this study was ~ $12,000. Wet chemical methods for CO_2 gas analysis are cumbersome and not as reliable.

SAFE OPERATIONS

The first lab meeting for this experiment, like all others in this course, concerns operational planning and a safety review. The safety review includes the following:

- **High pressure gas cylinders and regulators.** *For many students, this experiment is their first experience with gas cylinders and high pressure regulators. The instructor explains cylinders' and regulators' functions and operations. For both the CO2 and NH3 sources,students learn that these cylinders, both with reverse-threaded valve stem nuts, contain liquids under their own vapor pressures. The Joule-Thompson cooling that accompanies the vapor withdrawals is partly compensated for by using dual regulators in series. An analogy is drawn between such vapor withdrawal and that in a propane cylinder in a typical gas barbecue grill with which most students are familiar. Students are thus availed of a brief thermodynamics lesson.*
- **Gaseous ammonia leaks.** *The students are cautioned to avoid attempting to fix any NH_3 leak themselves. They are instructed to immediately notify the instructor or teaching assistant of any strong odor of ammonia. One such episode occurred in which a leak reported by students was traced to a cracked glass pipe that had been over-stressed during flange tightening.*
- **Personal safety equipment.** *Strict adherence to the safety goggle/glasses rule is required. Long pants and sensible shoes (no sandals, etc.) are required.*

OVERALL MASS TRANSFER COEFFICIENT

Aroonwilas, *et al.*[12] studied the overall mass transfer coefficient K_Ga_v (kmole/hr-m^3-kPa) for structured packing in CO_2 reactive absorbers. They found K_Ga_v is independent of gas flux, decreases with higher feed CO_2 content, and increases with higher liquid flux. Zeng, *et al.*,[2] using randomly dumped ceramic Raschig rings, observed K_Ga_v independent of CO_2 content, weakly dependent on liquid loading, strongly dependent on dissolved NH_3, with a mixed dependence on total gas flux.

In the current work, four series of experiments were carried out by an undergraduate student, as an independent study, to estimate the impact of key operating parameters on K_Ga_v. The data were analyzed using Eq. (3) to estimate K_Ga_v. Figure 2

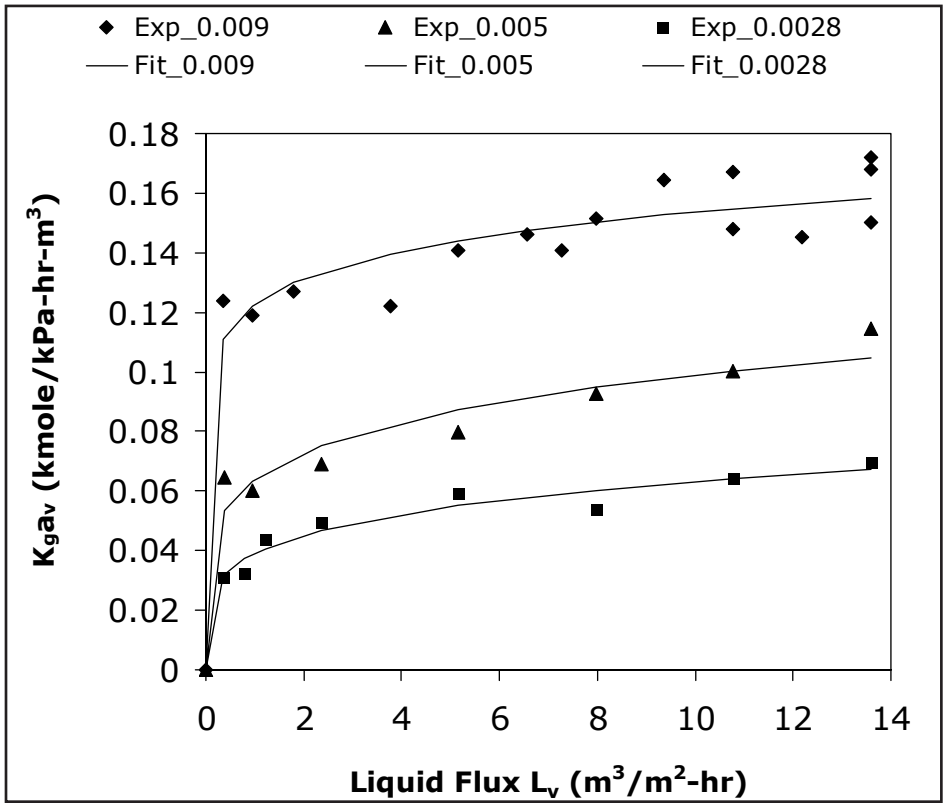

Figure 3. *Dependence of mass transfer coefficient on inlet liquid flux. Operating conditions: P_{CO2} = 9.5 kPa, V_t = 36 kmole/hr-m². Three different dissolved NH_3 mass fractions tested: 0.009, 0.005, 0.0028.*

shows that $K_G a_v$ has a fairly weak inverse dependence on total feed gas flux. Figure 3 shows that even a small liquid flux achieves some CO_2 absorption. A transient test wherein liquid flow starts in a dry column revealed rapid absorption. Figure 4 shows a weak inverse dependence on CO_2 feed partial pressure. Consistent with Zeng, *et al*., a fairly strong dependence on dissolved NH_3 concentration is shown in Figure 5 (page 112). The individual correlations for Figures 2-5 served as initial guesses for a single regression of the entire dataset:

$$K_G a_v = \frac{5.66 L_v^{0.15} C_{NH_3}^{0.73}}{P_{CO2}^{0.06} V_t^{0.10}} \qquad (5)$$

where P_{CO2} = the feed partial pressure of CO_2 (kPa), L_v = inlet volumetric liquid flux (m^3/m^2-hr), C_{NH3} = mass fraction of NH_3 in the feed liquid, and V_t = inlet total gas molar flux (kmole/hr-m^2). It is anticipated that specific constants in Eq. (5) might change values with a different packing. However, the general parametric trends will likely not.

DATA AND ANALYSIS

Eqs. (3) and (5) show how St offers a way to correlate all operational CO_2 capture data into a single relationship. An experimental database from students in the NJIT Chemical Engineering Lab II course was combined with the data collected for Eq. (5). For each experimental run, the St number was calculated using Eq. (5) and the left side of Eq. (3). Then, the righthand side of Eq. (3) was used to estimate the outlet CO_2 concentration, y_{exit}. Finally, this value was used with Eq. (4) to predict the CO_2 capture. This predicted capture was then compared to experimental data. These results are shown in Figure 6 (page 112). In general, good agreement was obtained using results based entirely on student data.

To fortify this correlation, an Analysis of Variance (ANOVA) was performed. It found that the experimental and predicted CO_2 captures for a fixed St were not statistically different. A simple average of calculated and observed captures is plotted, together with error bars, in Figure 6. A strong engineering correlation is obtained. A different correlation with similar characteristics would be obtained for a different random packing.

From a design perspective, Figure 6 can be used to help determine the size and/or operating parameters of a CO_2 scrubbing column packed with 1⁄2" berl saddles operating at room temperature (~ 23 °C). For example, assume a % capture must be achieved for a flue gas of designated rate and CO_2 concentration (y_o). Figure 6 provides the required St. The left side of Eq. (3), along with Eq. (5), can now be used together to estimate the needed operating parameters, most likely liquid and gas fluxes.

SUMMARY OF EXPERIENCES, ASSESSMENT, AND LEARNING

This experiment is performed within the ChE 496 – Chemical Engineering Laboratory II required capstone class. The course meets twice a week in 3-hour blocks. Once instructed in the safe operation of the system, a typical group of three students—usually seniors—can complete the required activities in 3-4 hours. Only one experimental system exists in our lab, being of pilot scale. Typically, it is operated 4-5 times per semester.

At the end of the laboratory course, students complete a survey for their comments on the specific experiments they executed. During Spring 2013, 14 students, working in groups, performed this new CO_2 capture experiment. Table 1 (page 97) presents an assessment of student responses to the survey questions. Table 2 (page 97) presents the student comments that were actually offered. On a 0 (lowest) – 4 (highest) scale,

the 14 students consistently ranked this experiment 3.5 or higher for both execution and analysis.

Students often anecdotally express their satisfaction with this experiment. Frankly speaking, the ammonia absorption that was replaced by this CO_2 scrubbing was seen as just another boring unit operation. The new experiment piques the students' interest. The current generation of students has grown up with global warming and the greenhouse gas issue. Some students seem to actually express a sense of pride in their environmental awareness while doing this experiment.

Considering the system complexity (review Figure 1), there was no surprise that several students commented (Table 2 and anecdotal) that, at first, they were intimidated. However, after a detailed orientation by the instructor, the students become more comfortable. By the time they had been collecting data for a while, most agreed that the system is actually easy to operate. In addition, some students expressed surprise at the HCl titrant volumes needed to neutralize even small volumes of the ammoniated water. Only then did they appreciate how strongly NH_3 is absorbed in water.

The current system allows for considerable flexibility in setting operating parameters. It has been observed that the smoothest student experience occurs by recommending a fixed ammoniated water concentration for a single laboratory class period. This is obtained by fixing the air, water, and NH_3 rates to either the wetted wall or upper packed columns. Due to the considerably lower surface area, the wetted wall yields a lower dissolved NH_3 concentration than the upper packed column. The students are encouraged to then vary individually the feed rates of air, CO_2, and ammoniated liquid (by varying the rate of liquid split off to drain) to the lower packed column. During the next laboratory period, students can repeat this exercise using a different dissolved NH_3 concentration by switching to the ammoniated water source that was not used the first time.

The data analysis, including the use of Eqs. (3)-(5), does present some conceptual challenges to the students. Using an earlier version of Eq. (5), they tried to predict the CO_2 capture for their particular column operating conditions, and then compare it to their measured capture. This leap is the biggest challenge for the students. Figure 6 offers an opportunity for students to witness the spread of real data that is behind most chemical engineering correlations. They see how use of a dimensionless number can provide a means to correlate different operational variables into a single relation!

Finally, assessment of student learning is done through the use of the

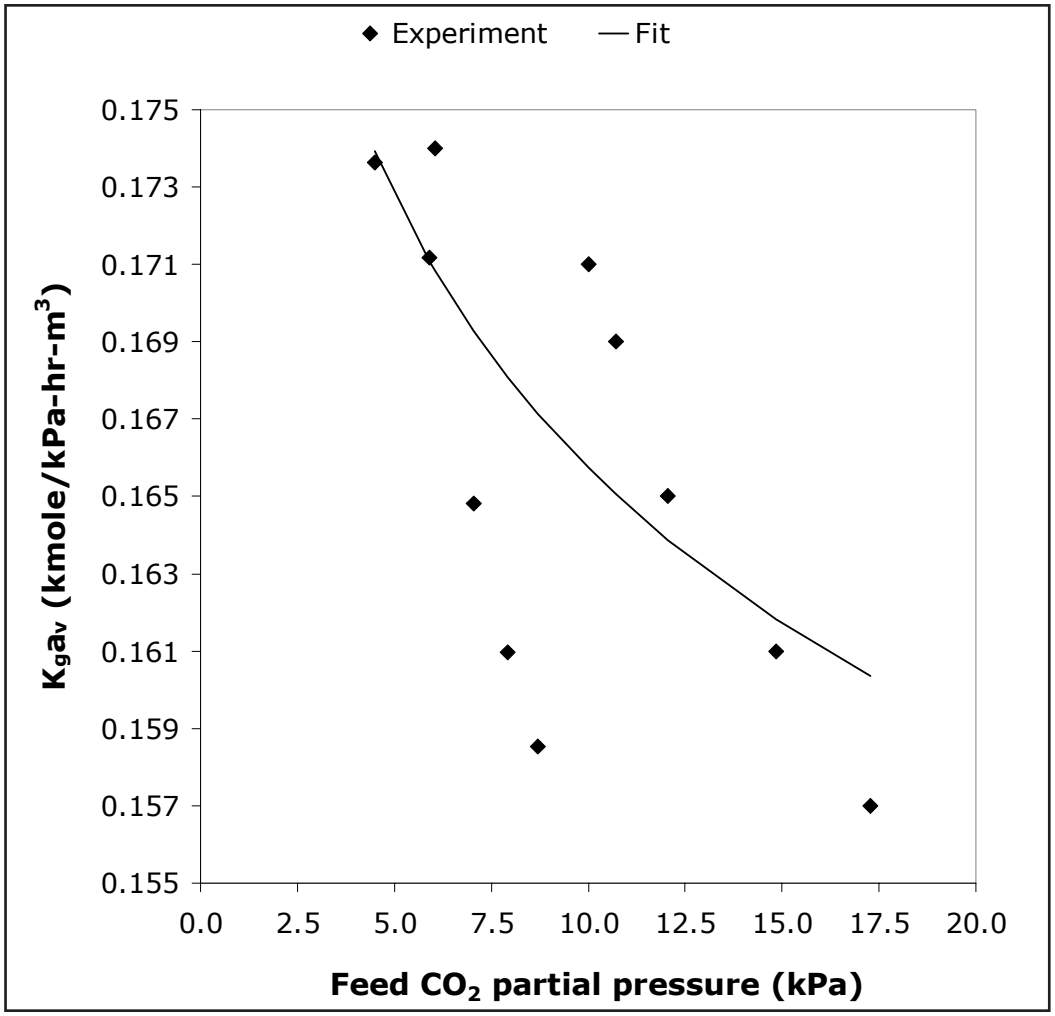

Figure 4. *Dependence of mass transfer coefficient on inlet CO_2 partial pressure. Operating conditions: C_{NH3} = 0.009 mass fraction, V_t = 39 kmole/hr-m^2, L_v = 13.6 m^3/hr-m^2.*

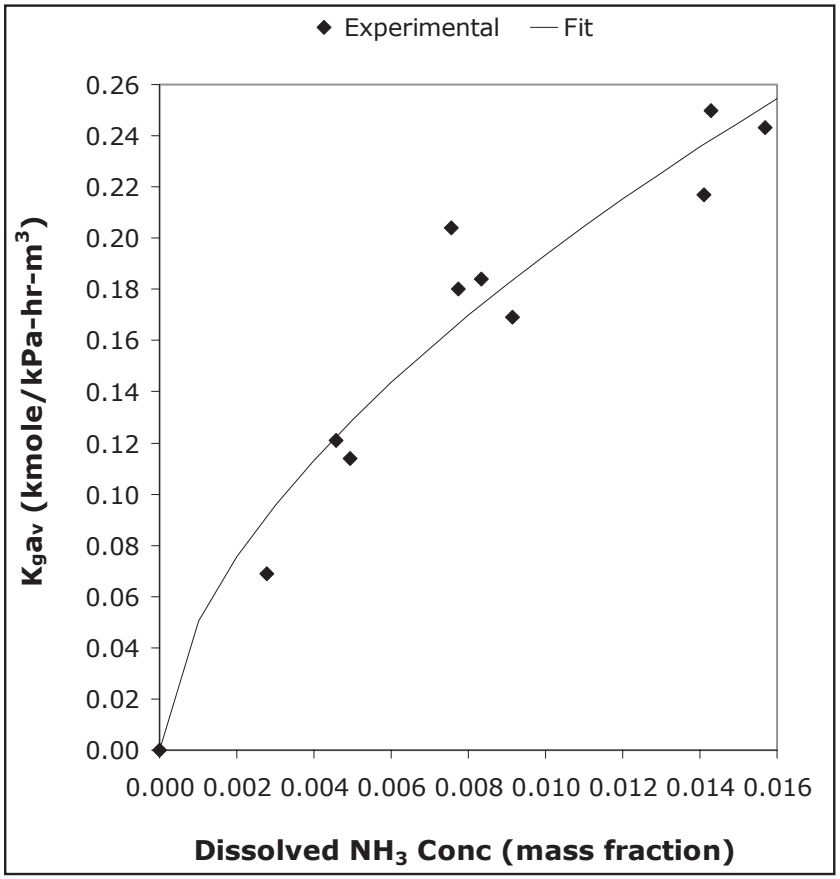

Figure 5. *Dependence of mass transfer coefficient on dissolved NH_3 concentration. Operating conditions: V_t = 36 kmole/hr-m², P_{CO2} = 9 kPa, L_v = 13.6 m³/hr-m².*

rubric presented in Table 3, page 97. A student group presents a draft report for preliminary, usually tough, grading. This is returned for editing and upgrading. A final draft is submitted, and subject to the same rubric. It is not unusual to see a large jump in the grade compared to the first draft.

CONCLUSIONS

Absorption of CO_2 from an air stream with aqueous NH_3 has been demonstrated in a packed column as an example of an effective "greenhouse gas" experiment for undergraduate lab. Since many labs already have a gas absorption unit operation, a retrofit is possible. Several operating parameters affecting CO_2 capture efficiency can be studied. A kinetic model offers an opportunity to correlate all data with a single integrated expression. This model gives rise to an engineering correlation for CO_2 capture efficiency as a function of a dimensionless Stanton number, thus providing a means to design such columns.

ACKNOWLEDGMENT

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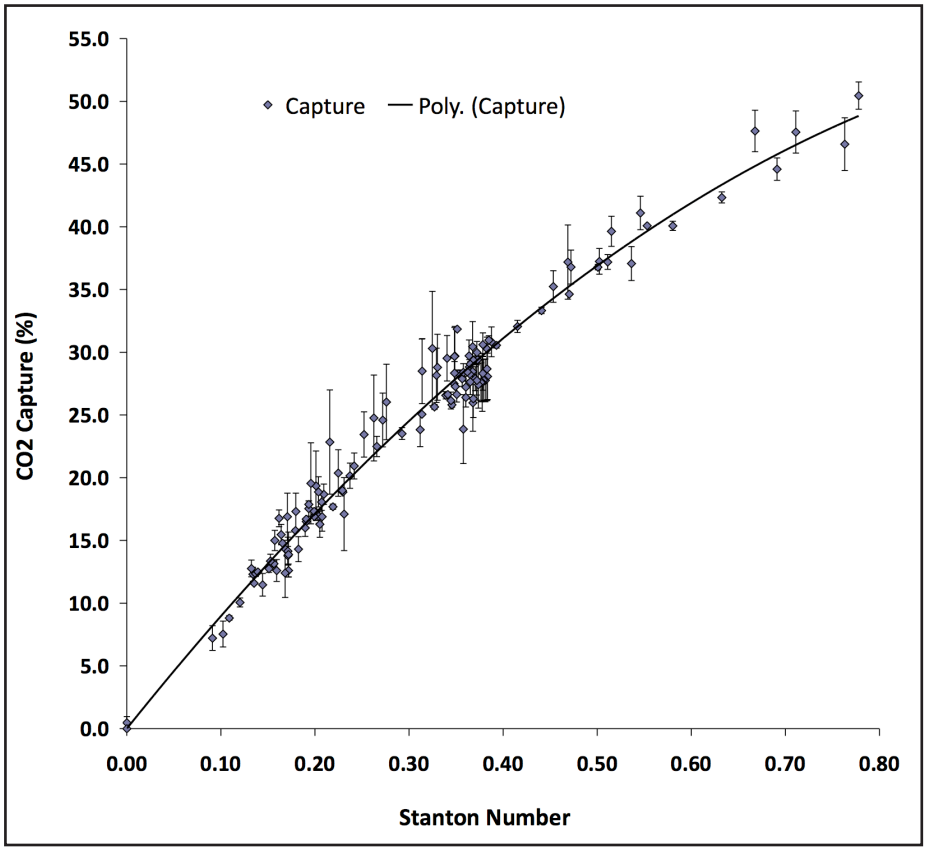

Figure 6. *Average CO_2 capture as a function of Stanton number, with uncertainty bars. Fit ($y \equiv$ Capture %, $x \equiv$ Stanton number): $y = -39.656\,x^2 + 93.626\,x$, correlation coefficient = 0.9738.*

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TABLE 1
Summary of Student Responses to Survey Questions on This Experiment

Equipment	0	1	2	3	4	WA
Quality of Operation			1	5	8	3.5
Analytical Components & Data Collection Quality				6	8	3.6
Modern and Efficient			1	5	8	3.5
Lab Manual Entry	**0**	**1**	**2**	**3**	**4**	**WA**
Theory			1	3	10	3.6
Procedure			1	3	10	3.6
Data Analysis				2	12	3.8

Total respondents: 14 Lowest score: 0 Highest score: 4 WA = weighted average

TABLE 2
Student Comments

"Very confusing to realize everything going on at once."
"Most difficult to set up, but a great lab to perform."
"Liked this lab – interesting."
"Need modernized controllers, or even just new valves."

TABLE 3
Rubric Used to Grade Student Reports and Assess Learning

NJIT Chemical Engineering Laboratory

Experiment:	**Student Names:**
Reporting Format:	**Draft (First / Final):**
Instructor:	**Date:**

No.	Review Questions	Poor	Fair	Good	Excellent
		1	2	3	4
1	Evidence of effective experimental planning				
2	Effective experimental execution				
3	Sufficient and quality data collected				
4	Correct theoretical model applied				
5	Comparison of model to experimental data				
6	Thorough presentation / discussion of results				
7	Insightful conclusions / recommendations				
8	Quality plots and tables				
9	Correct application of reporting structure				
10	Adequate reporting				
	Sub-Totals				
	Total Score (max 40 points)				

Comments: