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Stripper configurations for CO_2 capture by aqueous monoethanolamine and piperazine

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Abstract

Absorption/stripping with aqueous amines is a competitive technology for CO_2 capture from coal-fired power plants. A major challenge is reducing the energy requirement in the stripper, which has contributions from the reboiler(s), pumps, and compressors. In this study, the effects of flowsheet complexity and solvent choice were explored. Five flowsheets were stimulated in Aspen Plus® using 9 m MEA and 8 m PZ. Although the absorber was not modeled, the rich loadings used for the two solvents accounted for the faster CO_2 reaction rate of PZ in the absorber. The simulations demonstrated that increased configuration complexity improved the efficiency of the absorber by 5%-8%, depending on the solvent, operating temperature, and rich loading. The best improvement from the simple stripper was observed with the interheated column. The improvements were attributed to better reversibility of the more complex flowsheets. Furthermore, 8 m PZ consistently had a lower energy requirement than 9 m MEA. Configurations with packed columns exhibited improvements in energy consumption of 9%-11%.

Keywords: carbon dioxide; monoethanolamine; piperazine; stripper; complexity

1. Introduction

CO_2 capture is becoming an important topic to improve the environmental friendliness of heavily used energy sources like coal- and natural gas-fired power plants. Absorption/stripping by aqueous amines is considered the best option due to its proven applicability with the industry-standard solvent of monoethanolamine (MEA). Although 7 m MEA is proven technology, 9 m MEA has also been shown to be a feasible solvent [1]. Additionally, 8 m concentrated piperazine (PZ) is expected to improve overall performance with properties like higher resistance to oxidative and thermal degradation, higher reaction rate with CO_2, and more efficient stripping for regeneration [2]. In addition to the new solvent, advanced configurations have previously been explored [3]. The advanced configurations reduce energy usage by increasing the reversibility and decreasing the exergy loss [4]. The advanced

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process arrangements were used with a new model of concentrated PZ to determine the potential overall improvement over a base case with MEA.

2. Process Model

2.1. Thermodynamic model

A rigorous thermodynamic model was difficult to develop due to the large number of species present in the H_2O-PZ-CO_2 system, including a non-volatile zwitterion. A model for PZ has been developed [5], and its structure is based on the ΔG, ΔH, Cp, and τ method of specification in the electrolyte non-random two-liquid (e-NRTL) activity coefficient model used by Hilliard [6]. In the Aspen Plus® regression of this model, a large database of thermodynamic properties was used, including CO_2 solubility, amine vapor pressure, enthalpy of absorption, heat capacity, and NMR speciation.

2.2. Stripper representation

The simulations used Aspen Plus®, and their scope included the stripping vessels, rich and lean pumps, cross exchanger, and multistage, intercooled compressor. Several variables were held constant across all simulations to permit adequate comparison between solvents and configurations. The simulations were run with a constant rich CO_2 loading, and lean loading was varied and optimized. A 5°C cold side approach was specified on the main cross exchanger, and the reboiler(s) also had a 5°C approach. In configurations with multiple pressure stages, equal vapor production on a molar basis was maintained. By stipulating equal steps across the pressure stages, the most reversible operation was preserved to improve efficiency. Also in an effort to enhance reversibility, the analysis used a constant maximum temperature in the regenerator, which consequently resulted in variable pressures at different lean loadings. Finally, the outlet pressures of the pumps were specified to consistently account for frictional and gravitational losses in the pipes. These approximations considered 50 kPa of pressure drop in the cross exchange, and an appropriate amount of head to reach the elevation gain in configurations with packed columns.

Configurations with packed columns used a height of 5 m, which was enough packing to maintain a rich end pinch for all runs. Since all runs were pinched, they could be compared on a common level. IMTP#40 random packing was used with the Onda correlations for mass transfer coefficient and interfacial area and with the Chilton and Colburn correlation for heat transfer coefficient. Both of these correlations are standard options in Aspen Plus®. The reactions within the column were specified as equilibrium, assuming that the chemical reaction during desorption was fast enough that the mass transfer was the limiting step. The diameter of the column was always specified to have a maximum fractional capacity of 0.8. Configurations with flash tanks were modeled with thermal and chemical equilibrium.

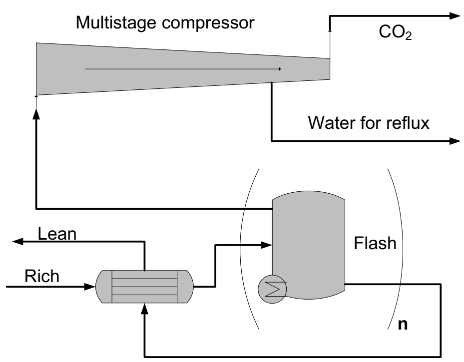

Figure 1: Multi-Stage Heated Flash (1SF and 2SF)

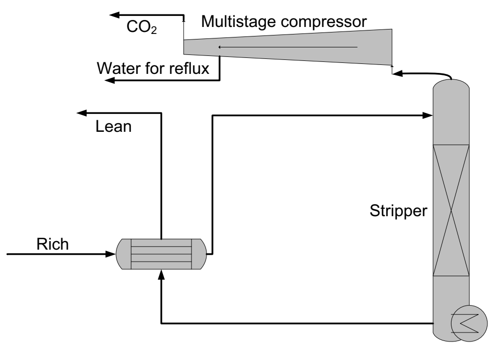

Figure 2: Simple Stripper (SS)

2.3. Configurations

The main goals of this study were to address the effect of configuration complexity on process efficiency and how this effect differed between MEA and PZ. Five configurations were explored, and they are described in Figures 1 to 4. The 1- and 2-stage flash configurations were derivations of the multi-stage flash arrangement (Figure 1). These configurations would be cheaper to construct as compared to the simple stripper (Figure 2). The adiabatic flash configuration (Figure 4) was an attempt to improve the efficiency of heat recovery by taking a small step down in pressure to approach absorber conditions, which consequently reduced the temperature and flashed off some CO_2 and water vapor. Without precooling, this low-pressure vapor was compressed to the main column pressure before returning it to the bottom of the stripper. This configuration introduced an additional pressure stage without adding an extra heating element. The interheated column also introduced complexity into the base case flowsheet (Figure 3). It had promise to improve the efficiency by approaching continuous heat exchange along the length of the packed column. The interheating occurred in the middle of the column and heated 80% of the solvent with an approach temperature of 5K. A continuously heated column would have the smallest exergy loss within the scope of the column itself.

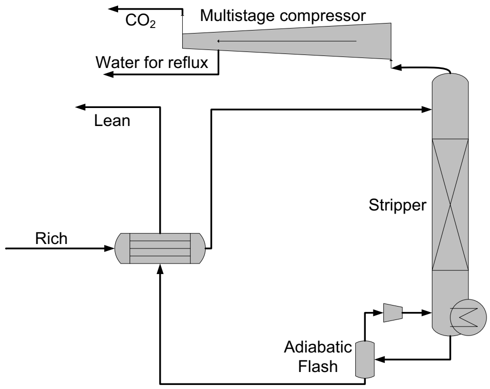

Figure 4: Packed Column with Adiabatic Lean Flash (ALF)

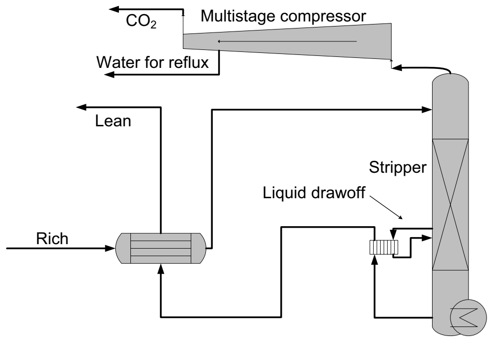

Figure 3: Interheated Column (IHC)

2.4. Absorber performance approximation

In order to appropriately compare the performance of the stripper using 9 m MEA and 8 m PZ, it was desired to determine a rich loading for each solvent which accounted for the difference in reaction rates in the absorber. The overall reaction rate constant k_g' combined the kinetic and mass transfer effects and can be used to calculate CO_2 flux with the gas side driving force between the bulk gas and interface concentrations:

$$N_{CO_2} = k'_g\left(P_{CO_2} - P^i_{CO_2}\right) \quad (1)$$

Data for k_g' in MEA and PZ was tabulated by Dugas [7] as a function of P^*_{CO2} at 40°C, which was directly indicative of the loading of the solution. The rate constant was also measured with varying temperature and solvent concentration, both of which had little effect (between 40°C and 60°C). This data was correlated to give k_g' as a function of P^*_{CO2} at 40°C for MEA using 40°C and 60°C data for 7 m, 9 m, 11 m, and 13 m MEA. A similar correlation was derived for PZ using 40°C and 60°C data for 2 m PZ, 5 m PZ, and 8 m PZ. The final correlation for each is shown below:

$$MEA: \quad \ln k'_g = -0.40 \cdot \ln P^*_{CO_2,40°C} - 14.35 \quad (2)$$

$$PZ: \quad \ln k'_g = -0.41 \cdot \ln P^*_{CO_2,40°C} - 13.44 \quad (3)$$

Next, corresponding rich and lean loadings sets for MEA and PZ were calculated which balanced the log mean fluxes, thereby indicating roughly equivalent absorber performance for the two solvents while using identical packing heights. Loading was defined in this work as the ratio of CO_2 moles per mole of alkalinity. This definition accounted for the presence of two amine groups on the PZ molecule. The lean loading was specified to match 10% of the rich equilibrium partial pressure since 90% removal in the absorber is expected.

Table 1: Rich and Lean Loadings for MEA and PZ to Match Log Mean Flux in Absorber

MEA rich		MEA lean		PZ rich		PZ lean	
P^*_{CO2} (kPa)	ldg	P^*_{CO2} (kPa)	ldg	P^*_{CO2} (kPa)	ldg	P^*_{CO2} (kPa)	ldg
5.0	0.50	0.50	0.45	8.4	0.42	0.84	0.33
1.5	0.48	0.15	0.40	5.0	0.40	0.50	0.31

Prior work [8] used a common rich and lean loading set for MEA corresponding to 5 kPa/0.5 kPa of P^*_{CO2} at 40°C. Table 1 shows that these loadings for MEA correspond to loadings for PZ which provide 8.4 kPa/0.84 kPa P^*_{CO2} at 40°C. It is expected that a more realistic loading set for PZ is 5 kPa/0.5 kPa, so this pair and the corresponding set for MEA will be used for the simulations. These estimates assume an isothermal absorber at 40°C.

2.5. Multistage compressor correlation

The multistage compressor block in Aspen Plus® (MCOMP) had convergence issues due to the high final pressure, small presence of solvent in the vapor, and use of the complex e-NRTL property method. To avoid its questionable behavior affecting the simulations, a correlation for the compressor work was separately developed to incorporate into the final energy requirement. An Aspen simulation with an isolated MCOMP block was run with the SRK property method and a feed consisting of CO_2 saturated with water at 40°C. Each vapor stream was intercooled to 40°C with water knockout between compression stages. The minor presence of solvent was ignored since it would have a negligible contribution to the total work requirement. The inlet pressure of the CO_2/H_2O mixture was varied from 0.8 to 20 bar. For each inlet pressure, the minimum number of compression stages was used to maintain a compression ratio no greater than 2. The outlet pressure was held constant at 150 bar. The compressor polytropic efficiency was taken to be 80%. The pressure drop per stage was assumed to be 20% of the suction pressure.

The final regressed form of the multistage compressor correlation was:

$$W_{comp}\left(\frac{\text{kJ}}{\text{gmol CO2}}\right) = \begin{cases} 4.572\ ln\left(150/P_{in}\right) - 4.096, & P_{in} \leq 4.56\ \text{bar} \\ 4.023\ ln\left(150/P_{in}\right) - 2.181, & P_{in} > 4.56\ bar \end{cases} \quad (4)$$

where P_{in} is the compressor feed vapor coming from the highest pressure stage in bar.

3. Results

Equivalent work was used to compare the performance between the different configurations and solvents. Equivalent work (kJ/gmol CO_2), calculated as in equation 5 below, uses the total heat duty (Q_i, in kJ/gmol CO_2), temperature of heat source (T_i), pump work, and compressor work to calculate a total work requirement on an electricity basis. The pumps and compressors would be run with electricity directly drawn from the power plant, and the reboiler(s) uses steam that could otherwise generate electricity in the plant turbines. The net work of the lean pump was neglected if the stripper pressure was higher than the required outlet pressure to pump the solvent back to the top of the absorber. The equation uses the 5 K driving force for the reboiler(s). The sink temperature (T_{sink}) was assumed to be 313K. Pump efficiency was 72%, and compressor work was calculated by equation 4.

$$W_{eq} = \sum_{i=1}^{n_{reboilers}} 0.75Q_i\left(\frac{T_i+5K-T_{sink}}{T_i+5K}\right) + W_{pumps} + W_{comps} \quad (5)$$

A numerical system was developed to rank the configurations by complexity level. The stripper section of each flowsheet was evaluated, and each of the following counted for one complexity point:

- Reboiler/heat exchanger
- Vessel
- Packing

The complexity levels for all configurations are listed in Table 2. As an example, the simple stripper had a complexity level of 3 because it contained one at each of the above complexity types: reboiler, vessel, and packing. The adiabatic lean flash had an additional credit over the other configurations because moving the first compressor stage down into the stripper eliminated the need for a precooler.

Table 2: Configuration Abbreviations and Complexity Levels

	Configuration	Complexity
1SF	1-Stage flash	2
SS	Simple Stripper	3
ALF	Stripper with adiabatic lean flash	3
2SF	2-Stage flash	4
IHC	Interheated column	5

3.1. MEA results

The 5 configurations listed in section 2.3 were evaluated using 9 m MEA. Simulations were run with two different rich loadings as suggested by section 2.4: 0.50 mol CO_2/mol MEA corresponding to 5 kPa P^*_{CO2} at 40°C, and 0.48 corresponding to 1.5 kPa P^*_{CO2} at 40°C. High temperature yields the best performance in the stripper due to greater CO_2 pressure, but the maximum temperature considered for MEA was 120°C due to elevated thermal degradation rates at higher temperatures [9]. Temperatures lower than 120°C were not of interest in this study, so only the reboiler temperature of 120°C was used for MEA. The work requirement and optimum lean loading for each configuration at the two rich loadings is detailed in Table 3.

Table 3: Work Requirement for Configurations Using 9 m MEA. Heating to 120°C and Lean Loading adjusted to minimize equivalent work.

Configuration	Equivalent Work	Lean Loading	Equivalent Work	Lean Loading
	kJ/mol CO_2	*mol CO_2/mol alk*	*kJ/mol CO_2*	*mol CO_2/mol alk*
	0.5 rich ldg		*0.48 rich ldg*	
1SF	34.9	0.41	37.2	0.39
SS	34.0	0.39	36.1	0.36
ALF	33.6	0.39	35.4	0.36
2SF	33.5	0.39	35.5	0.38
IHC	32.5	0.37	34.2	0.35

The lean loading was optimized for each configuration to minimize equivalent work. Every case demonstrated an overstripped optimum lean loading, where the P^*_{CO2} at 40°C was less than 10% of the rich equilibrium partial pressure. This result would be fortunate news for the design of the absorber because the lower lean loading would provide a greater driving force for absorption and reduce the size of the column. The best case scenario with a 0.5 rich loading improved the optimum performance of each configuration by 5% to 9%, with the greatest influence on the 2-stage flash. The performance typically improved with increased complexity. All configurations except the 1-stage flash showed improvement over the simple stripper base case. The best performance for both rich loadings was with the interheated column, demonstrating a 7.8% and 4.6% improvement over the simple stripper using rich loadings of 0.48 and 0.50, respectively.

3.2. PZ results

Similar to the MEA simulations, the 5 configurations were evaluated using 8 m PZ. PZ has a fast reaction rate with CO_2 and should be expected to achieve a high rich loading in the absorber. However, it was uncertain whether a rich loading with an equilibrium partial pressure higher than 5 kPa was feasible. Therefore, a rich loading of only 0.40, corresponding to 5 kPa P^*_{CO2} at 40°C, was used. PZ demonstrates a higher resistance to thermal degradation than MEA, and its ceiling temperature is 150°C [2]. It was also desired to observe the performance of PZ in a process designed for MEA with reboiler temperature(s) of 120°C. For these reasons, PZ was evaluated using 120°C and 150°C. The work requirement for each configuration at the two operating temperatures is detailed in Table 4.

Table 4: Energy Requirement with 8 m PZ. 0.4 Rich Ldg, 0.31 Lean Ldg (*= 0.28 Lean Ldg)

Configuration	Equivalent Work	
	kJ/mol CO_2	
T (°C)	*150*	*120*
1SF	36.1	39.2
SS	33.1	33.7
ALF	32.3	32.9
2SF	34.1	35.7
IHC	30.9*	31.8

The lean loading was optimized for each configuration. However, the optimal lean loading demonstrated understripping in many cases, where the P^*_{CO2} at 40°C of the solution with the optimal lean loading was greater than 10% of the rich equilibrium partial pressure. Some cases, particularly those with high complexity and/or high operating temperature, yielded a saturated optimum lean loading which was equal to the 90% removal spec. The only case which had an optimum lean loading that was overstripped was the interheated column at 150°C. The equivalent work reported for each configuration in Table 4 was for the saturated lean loading except for the interheated column at 150°C which had an optimum lean loading of 0.28. As described in section 3.1, optimum cases with overstripping would be ideal for the absorber to achieve the desired performance and rich loading. The improvement in the equivalent work between 120°C and 150°C was marginal, only 1% to 3% for the cases with optimized lean loadings, but the tabulated values with lean loadings at saturation or lower demonstrated a 2% to 8% improvement. Additionally, the reduced capital cost of the multistage compressor would favor operating at the elevated temperature of 150°C. The effect of complexity on the equivalent work was still noticeable, with a 5% and 6% maximum improvement over the simple stripper base case for 120°C and 150°C, respectively.

3.3. Comparison of MEA and PZ Performance

The use of 8 m PZ with a rich loading of 0.4 in the place of 9 m MEA with a rich loading of 0.48 yielded a 3%-11% improvement depending on the configuration. When changing only the solvent, the simple stripper showed the greatest improvement of 11%, followed by the interheated column with an improvement of 10%, and the adiabatic lean flash had the third-best improvement of 9%. The 1- and 2-stage flash configurations did not benefit much by using 8 m PZ, demonstrating only a 4% and 3% improvement, respectively. Table 5 summarizes the results of important solvent/configuration combinations. The total equivalent work was separated into its three components as used by equation 5: heating work, pump work, and compression work.

Table 5: Noteworthy Solvent/Configuration Combinations

System	Equivalent Work	Lean Ldg	Pressure	Reb duty	Q work	Pumps	Comp
	kJ/mol CO_2	*mol/mol*	*bar*		*kJ/mol CO_2*		
MEA - SS - 0.5 rldg	34.0	0.39	5.1	131	21.1	1.5	11.5
MEA - SS - 0.48 rldg	36.1	0.36	3.9	137	21.9	1.6	12.6
MEA - 2SF - 0.48 rldg	35.5	0.38	7.1 / 4.4	145	23.1	1.5	10.8
PZ - SS - 150C	33.1	0.31	9.3	112	22.6	1.5	9.0
PZ - 2SF - 150C	34.1	0.31	13.4 / 9.4	120	24.2	1.8	8.1
PZ - IHC - 150C	30.9	0.28	7.6	100	20.1	1.0	9.8

Various mechanisms within the stripper dictated the improvement of each combination. Changes in compression and pump work were straightforward. Compression work decreased due to any increase in the pressure of the vessel(s), and pump work increased due to any increase in the pressure of the vessel(s). However, pump work also decreased with reduced lean loading due to increased capacity and decreased solvent circulation rate. Several mechanisms directed changes in the heating work. First, increased reboiler temperature raised the heating work since the steam used would be of higher quality. Next, improved solvent capacity decreased the heat duty since less solvent would need to be heated to balance the temperature approach across the cross exchanger. Finally, the difference in the heats of desorption of CO_2 of the solvents would affect the amount of heat duty dedicated to desorption. The improvements of each combination in Table 5 can be explained using these mechanisms. 8 m PZ consistently performed better than 9 m MEA, mostly due to the fact that it could be operated at 150°C. At the higher temperature, the vessel pressures were significantly higher in the PZ cases, drastically reducing the compression work.

A comparison which demonstrated another major difference between the two solvents was the difference between the simple stripper and 2-stage flash. The flash configuration was capable of reducing the work requirement with MEA, but the performance worsened when transitioning from the simple stripper to 2-stage flash with PZ. Comparing the changes in work components for this modification with each solvent, it was apparent that PZ was not able to effectively use the 2-stage flash because it did not experience as significant of a drop in compression work as compared to MEA. Coupled with a slightly greater effect on both heat work and pump work, the 2-stage flash did not prove to be a better option with PZ. The Gibbs-Helmholtz relation suggests that the low heat of desorption of PZ yields a low CO_2 partial pressure in the stripper compared to an equal change in temperature with MEA. The partial pressure of water is roughly the same for the two solvents at equally high temperature, so the selectivity for CO_2 is lower with PZ than for MEA. Heat of desorption has previously been linked to improving performance for this reason [8]. Configurations using PZ need to effectively utilize the latent heat contained in the stripping steam which otherwise escapes with the CO_2, eventually becoming wasted heat as the steam is knocked out in the condenser preceding the multistage compressor.

Table 5 clarifies the source of improvement with the interheated column. First, since the heat contained in the lean stream was more effectively recycled to the column, the reboiler duty decreased, so the heating work also decreased. Next, the column pressure was lower with the lower lean loading, so the rich pump pressure change decreased by 15%. The lower optimum lean loading caused the solvent rate to decrease by 25%, so the overall decrease in rich pump work was 33%. The compression work increased by 9% due to the lower column pressure, but the other savings resulted in a much more efficient configuration.

Finally, the difference in optimum lean loadings between MEA and PZ needed to be addressed. As previously pointed out, the process optimally utilized overstripping for MEA, but only typically 90% removal for PZ. The rich loadings of 0.48 and 0.4 for MEA and PZ, respectively, were calculated to be an accurate comparison in section 2.4 when paired with the respective lean loadings corresponding to 90% removal. The magnitude of k_g' increases with decreasing loading. Since MEA optimized with lower lean loading, the log mean CO_2 flux in the absorber would be greater, so the rich and lean loadings for PZ needed to also be lower to similarly increase its log mean flux in the absorber. Table 6 summarizes the final set of rich and lean loadings for 9 m MEA and 8 m PZ. The optimized runs in section 3.1 demonstrated optimum lean loadings from 0.35 to 0.37, so a representative value of 0.36 was selected. The new calculated loadings for PZ were not significantly different than the originally selected values. Consequently, the simple stripper at 150°C had an energy requirement of 33.57 kJ/mol CO_2, only 0.4 kJ/mol CO_2 (1.4%) greater than the requirement with a rich loading of 0.4. Approximately the same change could be expected for the other configurations.

Table 6: Rich/Lean Loadings Accounting for Varying Reaction Rates

Solvent	Rich		Lean	
	P^*_{CO2} *(kPa)*	*ldg*	P^*_{CO2} *(kPa)*	*ldg*
MEA	1.5	0.479	0.09	0.360
PZ	4.5	0.394	0.45	0.308

4. Conclusions

With both MEA and PZ, greater complexity in the stripper usually resulted in better energy efficiency due to a closer approach to a reversible process. The improvement over the simple stripper depended on the solvent, rich loading, and reboiler temperature, but the interheated column consistently required 4.8% to 7.8% less equivalent work.

8 m PZ consistently had a lower energy requirement than 9 m MEA when using a rich loading which accounted for the faster reaction rate of PZ in the absorber. The simple stripper and complex configurations with packed columns demonstrated substantial improvement of 9%-11% better energy performance with PZ. The multi-stage flash configurations were 3%-4% better with PZ.

Increasing the stripping temperature of 8 m PZ from 120°C to 150°C reduced the work requirement by 1% to 3%.

Reducing the rich loading of the MEA runs to a more conservative value of 0.48 reduced the efficiency of each configuration by 2%-9%. The configuration least affected by the loading change was the interheated column.

5. Acknowledgments

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