

Alternative Stripper Configurations for CO₂ Capture by Aqueous Amines

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Aqueous absorption/stripping is a promising technology for the capture of CO₂ from existing or new coal-fired power plants. Four new stripper configurations (matrix, internal exchange, flashing feed, and multipressure with split feed) have been evaluated with seven model solvents that approximate the thermodynamic and rate properties of 7m (30 wt %) monoethanolamine (MEA), potassium carbonate promoted by piperazine (PZ), promoted MEA, methyldiethanolamine (MDEA) promoted by PZ, and hindered amines. The results show that solvents with high heats of absorption (MEA, MEA/PZ) favor operation at normal pressure. The relative performance of the alternative configurations is matrix > internal exchange > multipressure with split feed > flashing feed. MEA/PZ and MDEA/PZ are attractive alternatives to 7m MEA. The best solvent and process configuration, matrix with MDEA/PZ, offers 22 and 15% energy savings over the baseline and improved baseline, respectively, with stripping and compression to 10 MPa. The energy requirement for stripping and compression to 10 MPa is about 20% of the power output from a 500 MW power plant with 90% CO₂ removal. © 2007 American Institute of Chemical Engineers AIChE J, 53: 3144-3154, 2007

Keywords: monoethanolamine, stripper, carbon dioxide, simulation, piperazine, potassium carbonate, promoted MDEA, hindered amines

Introduction

The major challenge facing the implementation of aqueous absorption/stripping on a large-scale for CO₂ capture is the high capital cost (columns, pumps, exchangers, initial solvent) and operating cost (reboiler duty, pump circulation rate, solvent makeup) of the technology. If aqueous absorption/stripping technology is applied to a coal-fired power plant, the power output can be reduced by 20–40%. Current efforts to reduce the capital and operating cost include the development of alternative solvents to the industrial state-of-the-art, 7m (30 wt %) monoethanolamine (MEA), the use of innovative process configurations, flow sheet optimization, and energy integration with other sec-

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more complex configurations to reduce energy requirement

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tions of the power plant. Alternative solvents should provide equivalent or greater CO₂ absorption rates than MEA, adequate capacity for CO2 and reduced cost of regeneration. The important alternative solvents include promoted and mildly hindered amines including the proprietary solvent KS-1. 11,12

Alternative process configurations have also been proposed

to reduce capital and operating costs of the CO2 capture pro-

for CO₂ removal.

cess. Some configurations, such as the use of multiple absorber feeds and split flow, have been proposed for the gas sweetening industry. ^{13,14} The performance and cost structure of the split flow configuration has been evaluated by Aroonwilas and Veawab. 15,16 Oyenekan and Rochelle 17,18 have evaluated vacuum and multipressure configurations, and Jassim and Rochelle¹⁹ have evaluated multipressure stripping with vapor recompression. Leites et al.20 proposed other

In this work, an evaluation of four new stripper configurations (matrix, internal exchange, flashing feed, and multipressure with split feed), with seven representative solvent profiles is presented. The solvent properties are approximate and are not necessarily accurate representations of specific solvents, but can be viewed as generic surrogates. The stripper model is equilibrium based and does not include absorber modeling and economics.

Analysis of the baseline configuration

Our previous work¹⁷ suggests the optimum generic solvent at 160 kPa (normal pressure) is one with a higher heat of desorption than 7m (30 wt %) MEA. Since PZ/K₂CO₃ solvents have heats of desorption lower than 7m MEA, they cannot be employed in a simple stripper with lower energy requirement than 7m MEA. The PZ/K₂CO₃ solvents possess some characteristics that may be exploited in optimized configurations. These include a lower heat of desorption, which lends itself to better isothermal system operation and stripping at vacuum. The faster rates of reaction with CO₂ permit richer solutions than MEA. Since piperazine is not subject to the same chemistry of thermal degradation as MEA, it may be possible to operate the stripper at a much higher-temperature and pressure than MEA. This will reduce the reboiler duty and total equivalent work, because of the greater temperature swing giving an effect of a solvent with a higher-heat of desorption. Some results from our earlier study¹⁷ are summarized in the following.

Temperature Approach in the Cross Exchanger. Our previous work¹⁷ showed that a 5 K approach in the cross exchanger requires less total equivalent work for stripping than a 10 K approach at the expense of capacity. At a given reboiler pressure, operating at a 5 K approach gives a higher temperature at the top of the column than a 10 K approach. The temperature change across the stripper is also smaller and the reboiler duty is reduced. Achieving a 5 K approach on the hot side of the cross exchanger may require a small fraction of the rich solution from the absorber to bypass the cross exchanger, and be directly heated by exchange with the stripper overhead vapor, because of differences in the heat capacities of the rich solution to the stripper, and the lean solution from the stripper.

Rich End Pinching. The stripper operation is frequently determined by a rich end pinch, because of the larger L/G ratio at the top of the column relative to that at the bottom. With rich end pinches, the driving force at the lean end is excessively large with a loss of available work. There may be configurations that will result in an equally distributed driving force from the rich to the lean end, and, therefore, reduce reboiler duty and total equivalent work.

Latent Heat Loss in Stripper Overhead. Typically, the stripper overhead includes 0.5 to 2 moles of water vapor/ mole CO₂. If this stream is condensed with cooling water, the latent heat of water vapor in the stream is lost. It would be beneficial if this heat could be recovered. The simple and vacuum configurations do not recover this heat, but the multipressure system¹⁷ does. The new configurations in this work also recover this heat.

Alternative Solvent Types

The stripper configurations were evaluated with seven sets of solvent properties. The solvent properties were obtained as approximate representations of specific solvent alternatives. These generic solvents may be poor representations of the specific solvent alternatives from which they are derived. The generic solvents give specific heats of absorption $(\Delta H_{\rm abs})$, capacity, and rates of reaction with CO₂. The vaporliquid equilibrium (VLE) representation of the solvents was obtained from various sources. 2,21-23 A greater heat of desorption will increase the reboiler duty required to reverse the reaction, but it also reduces the reboiler duty required for stripping steam by increasing the CO₂ equilibrium vapor pressure. In order to accurately address this tradeoff it is critical that the heat of desorption is consistent with the representation of the VLE. Therefore, the heat of desorption was obtained by differentiating the VLE expression with respect to the inverse of temperature. This approach will produce a heat of desorption that may not be consistent with other calorimetric data or theoretical expectations.

Moles of Alkalinity (mol Alk) is given by

Potassium Carbonate/Piperazine. This class of solvents proposed by Cullinane² takes advantage of the fast reaction rates of CO₂ with piperazine (PZ), and the low heat of CO₂ desorption from potassium carbonate (K₂CO₃). The most studied formulation has been 5m K⁺/2.5m PZ. This formulation and 6.4m K⁺/1.6m PZ have been studied at the pilotscale.²⁴ A third formulation, 4m K⁺/4m PZ, is proposed because it will provide greater capacity for CO₂ absorption. The vapor-liquid equilibrium (VLE) representation of the solvents was obtained by fitting points calculated by the thermodynamic model of Cullinane² to a six parameter expression.

Promoted MEA. The reaction rates of CO2 with MEA can be enhanced by the addition of piperazine. 6,7,25 In this work, CO2 solubility in 7m MEA/2m PZ has been represented by the surrogate solvent 11.4m MEA.

Promoted Tertiary Amines. Tertiary amines, such as methyldiethanolamine (MDEA) have been used in natural gas processing for decades. MDEA has a high-capacity for CO₂ absorption and requires low-regeneration energy. However, it has slow rates of CO2 absorption. To make MDEA attractive for CO₂ capture, it can be promoted by PZ. 8,26-28 In this work, the solubility of CO₂ in MDEA promoted by PZ is represented by the solubility of CO₂ in 4.28M (50 wt % or 8.39m) MDEA.

Hindered Amines. This class of solvents has been found to possess adequate rates of reaction with ${\rm CO_2}$, good ${\rm CO_2}$ capacities, and low-heat of regeneration. ^{29–32} In this work, KS-1 at 8.39m is used as a representative hindered amine solvent with limited equilibrium data extracted from Mitsubishi publications.³⁰

Alternative Configurations

Figures 1 to 4 show four configurations that minimize energy requirement for stripping. The energy requirement is minimized at the expense of increased capital cost and process complexity. Each of these configurations assumes appro-

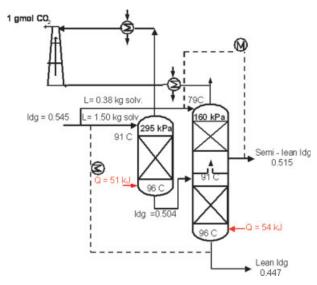


Figure 1. Double Matrix (295/160 kPa) Stripper for MEA/PZ (Liquid rate = 1.88 kg solvent, Rich loading = 0.545 mol CO₂/mol Alk, lean loading = 0.447 mol CO₂/mol Alk, $\Delta T = 5$ K).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

priate cross-exchange of the hot lean stream(s) with the cold rich stream(s) with an approach temperature of 5 K on the hot side. Each box represents a countercurrent packing section of gas/liquid contacting.

Matrix Stripper. In this two-stage matrix (Figure 1), the temperature change across the stripper is reduced as in the multipressure configuration but without the inefficiencies associated with mechanical compression. The rich solution

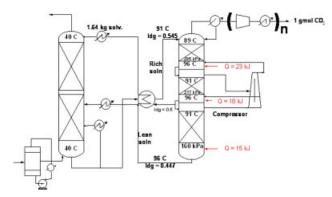


Figure 3. Multipressure with Split Feed Stripper (295/ 217/160 kPa) for MEA/PZ (Rich loading = 0.545 mol CO₂/mol Alk, lean loading = 0.447 mol CO₂/mol Alk, $\Delta T = 5$ K).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

from the absorber is split into two streams. The first is sent to the first stripper at a higher pressure resulting in a slightly superheated feed. Heat is applied in the form of reboiler steam. The lean solution from the first column is the semirich feed to the middle of the second column (which operates at a lower pressure). The other rich stream is fed to the top of the second stripper. The second column produces a semilean and a lean stream. The semilean stream is crossexchanged with the rich feed to the second column, while the lean solution is cross-exchanged with the rich solution to the first stripper. The water vapor from the overhead of the second column is condensed, and the CO2 is sent to the first

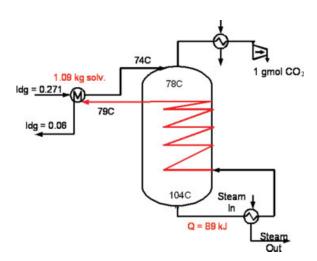


Figure 2. Internal Exchange Stripper at 160 kPa for MDEA/PZ (Liquid rate = 1.09 kg solvent, Rich loading = 0.271 mol CO₂/mol Alk, lean loading = 0.06 mol CO₂/mol Alk, $\Delta T = 5$ K).

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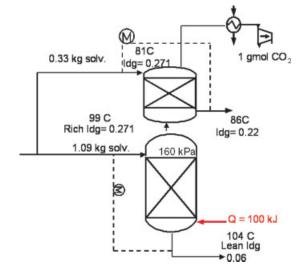


Figure 4. Flashing Feed Stripper at 160 kPa for MDEA/ PZ (Rich loading = 0.271 mol CO₂/mol Alk, lean loading = 0.06 mol CO₂/mol Alk, ΔT = 5 K).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 1. VLE Expression for PZ/K2CO3, MEA, and Promoted MEA

	$\ln P_{\text{CO}_2}^* = a + b\gamma + \frac{c}{T} + d\frac{\gamma^2}{T^2} + e\frac{\gamma}{T^2} + f\frac{\gamma}{T}$						
	6.4m K ⁺ /1.6m PZ	5m K ⁺ /2.5m PZ	4m K ⁺ /4m PZ	7m MEA	MEA/PZ (11.4m MEA)		
A	-19.49	-4.59	12.088	35.11	30.27		
В	24.46	34.21	42.39	-45.04	-38.87		
C	3435.22	-3834.67	-7087.74	-14281	-11991		
D	1464774	-1747284	-925155	-546277	1110073		
E	-5514009	-1712091	1393782	-3400441	-4806203		
F	12068.45	8186.474	-8552.74	32670.01	31355.6		
R square	0.995	0.992	0.984	0.997	0.995		
Ref.		2			21		

stage of the compression train. The water vapor in the overhead from the first column is condensed, and the CO₂ is sent to the second stage in the compression train.

The compression work in this configuration is reduced because some of the CO₂ is recovered at a higher pressure, therefore requiring less compression downstream. The lower pressure column is set to 160 kPa for normal pressure operations, and 30 kPa for vacuum operations. The pressure of the higher-pressure column and the flow into the flash section are optimized to minimize the total equivalent work of the system. Even though a two-stage matrix is described in this work, a three-stage matrix can also be used with reduced energy requirement but increased complexity.

Internal Exchange Stripper. This configuration (Figure 2) integrates the stripping process with heat transfer. It serves to approach the theoretical limit of adding and removing material and energy streams along the entire column. This process has been described by Leites et al. 20 It is approximated in a configuration tested by Mitsubishi. 12 The configuration alleviates the temperature drop across the stripper by exchanging the hot lean solution with the solution in the stripper. One implementation would place continuous heat exchange surface in the stripper, so that there is countercurrent heat exchange of the hot-lean solution, with the solution coming down the stripper. A large overall heat transfer capability of 41.84 W/K-mol solvent per segment was used. This gave a typical ΔT of 1.2 K and 3 K in the internal exchanger for the vacuum operation, and for operation at normal pressure, respectively.

Multipressure with Split Feed. The multipressure configuration was described in our previous work.^{17,19} This advanced configuration (Figure 3) takes a 10% split feed from the liquid flowing from the middle to the lowest pressure level in a multipressure stripper, and sends this stream to an appropriate point in the absorber. The temperatures at the bottom of the stripper pressure sections are equal, and heat is added to each stripper pressure section to achieve isothermal operation in each section, so that irreversibilities and work loss are reduced. This configuration takes advantage of the favorable characteristics of the multipressure configuration and the split flow concepts. The top pressure has been optimized for all solvents and configurations. The middle pressure was taken as the geometric mean.

Flashing Feed Stripper. This configuration (Figure 4) is a special case of the split flow concept described by Leites et al.²⁰ and Aroonwilas.¹⁵ A fraction of the rich stream is sent to the middle of the stripper, where stripping occurs

and a lean solution exits at the bottom. The rich solution is cross-exchanged with the lean solution exiting the stripper bottom. The vapor leaving the stripper is then contacted with the absorber rich flow in a five-staged upper section where the latent heat of water vapor is used to strip the CO_2 in the "cold feed" and a semilean stream is produced. The semilean product is cross-exchanged with the rich solution fed to the upper section. The reboiler duty remains unchanged, and "free stripping" can be achieved in the upper section. The split ratio of the rich streams into the middle and upper sections was optimized to minimize equivalent work.

Model Development

An equilibrium stripper model for aqueous solvents developed in Aspen Custom Modeler (ACM) was used to evaluate the different process configurations and solvents. A rich end pinch is usually predicted because of the generous amount of contacting assumed in the model. The stripper consisted of a flash region, 10 segments with 40% Murphree efficiency assigned to CO₂, and a reboiler with 100% CO₂ efficiency. The flash region in the column was quantified in terms of actual section performance.

Modeling Assumptions

- The sections are well mixed in the liquid and vapor phases.
- 2. The reboiler is in vapor/liquid equilibrium.
- 3. There is negligible vaporization of the amine.

The CO_2 vapor pressure (kPa) under stripper conditions for 7m MEA, promoted MEA and different PZ/K_2CO_3 blends is represented by the empirical expression in Table 1. The adjustable constants in Table 1 for the PZ/K_2CO_3 solutions were obtained by regressing points from the rigorous thermodynamic model by Cullinane. The constants for the MEA solvents were regressed from points obtained from equilibrium flashes in AspenPlus using the electrolyte non random two liquid (E-NRTL) model developed by Freguia from data of Jou et al. 33

The CO₂ vapor pressure over 4.28M MDEA and KS-1, based on the model by Posey et al. ²² is shown in Table 2. For 4.28M MDEA, the constants in Table 2 are taken from Posey et al. For KS-1 the constant, A, was set at 32.45, while constants B-D, in the equilibrium constant expression were adjusted to fit available data. ³¹ The amine mole fraction

Table 2. VLE Expression for Promoted MDEA and KS-1

	$P^*_{\text{CO}_2} = K_{\text{CO}_2} X_{\text{CO}_2}$ $\ln K_{\text{CO}_2} = A + \frac{B}{T} + C \gamma X^{\text{o}}_{\text{amino}}$	
	MDEA/PZ (4.28 M MDEA) (8.39 m MDEA)	KS-1 (8.39 m amine)
A	32.45	32.45
В	-7440	-8870
C	33	52
D	-18.5	-15
$X_{\rm amine}^{\rm o}$	0.1313	0.1313
Ref.	22	23

shown in Table 2 for KS-1 is set at 0.1313. The fit of the KS-1 data is shown in Table 3. The CO_2 solubility in the different solvents at 313 K is shown in Table 4.

The heat of desorption was calculated by differentiating the equation in Table 1 with respect to 1/T

$$-\frac{\Delta H}{R} = c + 2d\frac{\gamma^2}{T} + 2e\frac{\gamma}{T} + (f \gamma)$$
 (2)

where ΔH is the heat of desorption, R is the universal gas constant, T is the temperature in K, γ is the CO₂ loading, and c,d,e,f are empirical constants.

The heat of desorption for 4.28M MDEA and KS-1 was assumed to be constant at 62 and 73 kJ/gmol CO₂, respectively. The heat of vaporization of water, partial pressure of water, and heat capacities of solvent (assumed to be water), steam, and CO₂ were calculated with equations from the DIPPR database.³⁵ The molar heat capacities for the CO₂, water and amine were assumed to be equal and set to that of one mole of water.

Table 4 gives calculated values of the heat of CO_2 desorption with rich and lean loading at absorber (40°C) and stripper (100°C) conditions. The greatest variation of the heat of desorption (30 to 62 kJ/gmol) occurs with 6.4 m K⁺/1.6 m PZ. The variation of the heat of desorption with loading and temperature is not always in the expected direction with loading and temperature, but it is thermodynamically consistent with the representation of the VLE for these solvents. The average heat of desorption probably represents its effect on the VLE and the amount of stripping vapor required. The value at the stripper conditions probably represents its effect on the reboiler duty required to reverse the reaction. To the extent that these values do not represent the true solvent, the results in this article represent hypothetical solvents.

The partial pressure of CO_2 and water in each section was calculated by

$$P_n = E_{\text{mv}}(P_n^* - P_{n-1}) + P_{n-1}$$
(3)

A Murphree efficiency $(E_{\rm mv})$ of 40 and 100% was assigned to ${\rm CO_2}$ and water. The model assumed that temperature equilibrium is achieved in each section.

The model inputs were the rich loading and liquid rate, the temperature approach on the hot side of the cross exchanger (difference between the temperature of the rich stripper feed and the lean solution leaving the bottom of the stripper), and column pressure. Initial guesses of the lean loading, section temperatures, partial pressures, and loading were provided. The model solves equations for calculating VLE, and for material and energy balances. It calculates temperature and composition profiles, reboiler duty, and equivalent work.

The total energy required by the stripper is given as total equivalent work

$$W_{\rm eq} = 0.75Q \left[\frac{(T_{\rm reb} + 10) - 313}{(T_{\rm reb} + 10)} \right] + W_{\rm comp}$$
 (4)

 $W_{\rm comp}$ constitutes the isentropic work of compression to 330 kPa of the gas exiting the top of the stripper. An efficiency of 75% was assumed for the compressor. For the vacuum operations, five compressor stages were used, while for the normal pressure cases, three compressor stages were used. Two stages of compression were used to get to the maximum pressure of the process and an additional stage to 330 kPa with intercooling to 313 K between compressor stages.

The work lost by extracting steam from the power plant, which would have been used to drive turbines to generate electricity, is the first term on the righthand side of Eq. 4, while the second is the compressor work. The condensing temperature of the steam is assumed to be 10 K higher than the reboiler fluid. The turbine assumes condensing steam at 313 K, and has been assigned an effective efficiency of 75%.

Results and Discussion

Table 5 gives the performance (stripping and compression work to 330 kPa) of the stripper configurations investigated, and the capacities of the solvents to achieve 90% CO₂ removal. The rich $P_{\text{CO}_2}^*$ shown in the table are approximate rich partial pressures expected for the solvents investigated. 4m K⁺/4m PZ, MEA/PZ, and MDEA/PZ are assigned greater rich $P_{\text{CO}_2}^*$, because they are solvents with faster rates of reaction with CO₂, which should result in richer solutions with a fixed absorber size. The values of $P_{\text{CO}_2}^*$ (5 and 7.5 kPA) result in unexpectedly high rich loading with the MEA solvents. This absorber performance may require the use of more complex absorber designs with intercooling and increased packing height and surface area.

In this work, the lean loading for each configuration was optimized to minimize equivalent work. The optimum lean loading, the lean loading that minimized equivalent work, was quite flat for cases with $\Delta T=5$ K, and was approximately that for 90% change in equilibrium partial pressure of $\rm CO_2$ from the absorber rich end to the absorber lean end at

Table 3. Fit of KS-1 VLE Data

		KS-1 data ²³	Model
T(K)	CO ₂ loading	$P_{\mathrm{CO}_2}^*$	(kPa)
313.15	0.375	0.7	1.0
	0.45	1.8	2.0
	0.5	3.1	3.0
	0.575	7.6	5.9
393.15	0.05	3.8	3.3
	0.0625	5.5	4.9
	0.21	51.7	57.3
	0.325	248.2	189.1

Table 4. Results Calculated from the Equilibrium Models

	a. Equilibrium CO ₂ loading (mol/mol Alk) at 313 K							
P_{CO_2} (kPa)	6.4m K ⁺ /1.6m PZ	5m K ⁺ /2.5m PZ	4m K ⁺ /4m PZ	7m MEA	MEA/PZ (11.4m MEA)	MDEA/PZ (8.4 m MDEA)	KS-1 (8.4 m amine)	
0.125	0.468	0.416	0.322	0.373	0.363	0.019	0.177	
0.5	0.532	0.467	0.384	0.442	0.428	0.046	0.303	
0.75	0.549	0.482	0.402	0.463	0.447	0.060	0.345	
5	0.627	0.560	0.493	0.563	0.528	0.213	0.556	
7.5	0.643	0.578	0.514	0.586	0.545	0.2701	0.602	
10	0.654	0.592	0.529	0.602	0.556	0.317	0.633	
	b. Calculated I	Heat of CO ₂ Desorption	on (kJ/gmol CO ₂), I	Rich loading at	$P_{\rm CO_2}$ given in Tab	ole 5, Lean loading a	t $0.1 P_{\rm CO}$,	
			Absorber at	40°C, Stripper	at 100°C		_	
Rich Abs	62	74	70	77	80	62	73	
Rich Strip	37	61	74	59	61	62	73	
Lean Abs	52	63	66	84	86	62	73	
Lean Strip	30	53	69	70	69	62	73	
Average	45	63	70	73	74	62	73	

313 K. The cases with an approach temperature of 10 K frequently resulted in greater that 90% change in equilibrium partial pressure (overstripping) from the absorber rich to lean ends.

In all of the cases with a 5 K approach temperature, the optimum lean loading was quite high.

The heat of absorption shown in Table 5 is the average value from Table 4.

The capacity of the solution is given by

$$capacity \left(\frac{mol\ CO_2}{kg\ H_2O}\right) = (\gamma_{rich} - \gamma_{lean}) \frac{mol\ Alk}{kg\ H_2O} \tag{5}$$

Effect of Varying Temperature Approach. The "baseline" configuration for each system given in Table 5 is a simple stripper operating at 160 kPa, with a 10 K approach on the hot side of the cross exchanger. Table 5 also gives the energy requirement for an "improved baseline" with a 5 K approach. The lean loadings for the baseline ($\Delta T = 10 \text{ K}$) were optimized, and frequently resulted in overstripping which increases the capacity of the solvents for absorption. With a 5 K approach on the hot side of the cross exchanger, 3 and 12% reduction in equivalent work was obtained for the 6.4m K⁺/1.6m PZ and 7m MEA solvents, respectively, relative to the baseline case with a 5 K approach with these

Table 5. Predicted Performance of Different Solvents Using Various Stripper Configurations (90% removal, $\Delta T = 5 \text{ K}, P_{\text{final}} = 330 \text{ kPa})$

Solvent		6.4m K ⁺ /1.6m PZ	5m K ⁺ /2.5m PZ	4m K ⁺ /4m PZ	7m MEA	MEA/PZ	MDEA/PZ	KS-1
$\Delta H_{\rm abs}$ (kJ/gmol CO ₂)		45	63	70	73	74	62	73
Rich $P_{\text{CO}_2}^*$ (kPa) at 3	313 K	5	5	7.5	5	7.5	7.5	5
Capacity (mol CO ₂ /l		0.91	0.93	1.34	0.85	1.12	1.77	2.11
Configuration	Pressure (kPa)		Eq	uivalent Work (kJ/	gmol CO ₂)			
Baseline	$160 (\Delta T = 10 \text{ K})$	28.1	24.9	21.4	22.3	20.0	18.3	19.1
Improved Baseline	160	27.4	22.6	19.0	19.7	17.5	17.2	17.9
Multipressure	x/160	27.0	20.5	17.8	18.2	16.2	16.3	17.0
•	X	180	265	295	280	295	295	295
Matrix	x/160	24.3	21.7	15.6	18.0	15.7	15.1	16.1
	X	250	295	295	265	295	295	295
	Feed split (%)	120	40	20	25	25	30	30
Internal Exchange	160	25.3	19.5	17.3	17.5	16.0	15.7	16.5
Multi P with 10% sp	olit feed	29.7	20.7	17.5	18.1	15.9	15.7	16.6
Flashing feed	160	23.5	20.7	18.0	18.7	16.8	16.3	17.2
	Feed split (%)	85	35	20	25	20	30	35
Vacuum	30	23.7	23.1	21.1	22.6	21.1	19.8	21.2
Multipressure	x/30	23.7	22.5	20.2	21.6	19.9	19.2	20.7
-	X	30	42	45	45	47	45	42
Matrix	x/30	22.5	21.8	18.1	21.2	19.4	18.2	19.8
	X	42	45	47	47	45	45	45
	Feed split (%)	90	55	40	50	35	40	70
Internal Exchange	30	22.5	21.6	19.8	21.0	19.8	19.0	20.4
Multi P with 10% sp	olit feed	31.3	22.6	20.2	21.6	19.7	19.9	20.7
Flashing feed	30	22.7	22.5	20.6	22.1	20.6	19.5	20.8
-	Feed split (%)	55	35	35	35	30	35	45

x = highest pressure in configuration.

Table 6. Contributions to Reboiler Duty—Effect of Temperature Swing on Simple Strippers

	6.4m K ⁺	/1.6m PZ	MEA	A/PZ
P (kPa)	30	160	30	160
$\left(\frac{P_{\text{CO}_2}}{P_{\text{H}_2\text{O}}}\right)$ at rich end	0.538	0.415	1.065	1.850
$\Delta H_{\rm des}$ (kJ/gmol CO ₂)	51	34	76	68
$\left(\frac{n_{\text{H}_2\text{O}}}{n_{\text{CO}_2}}\right) \text{ H}_{\text{vap}} \text{ (kJ/gmol CO}_2)$	81	105	41	24
$\left(\frac{L Cp \Delta T}{n_{\text{CO}_2}}\right)$ (kJ/gmol CO ₂)	30	30	24	24
Q (kJ/gmol CO_2)	162	169	141	115

solvents. This savings in energy would be at the expense of a larger investment in heat exchange surface.

Effect of Operating Pressure. Operating the stripper atrocuum (30 kPa), with a 5 K temperature approach in the cross exchanger, offers a 14% reduction in equivalent work for 6.4m K⁺/1.6m PZ and 4 and 20% more energy with 5m K⁺/2.5m PZ and MEA/PZ, respectively. This shows that vacuum operation favors solvents with low heats of absorption, while operation at normal pressure favors solvents with high heats of absorption. This effect was also confirmed in the results with a generic solvent, reported in the next section. Solvents with high heats of absorption take advantage of the temperature swing. The relative vapor pressure of CO₂ and water changes with temperature. This change is greater with solvents with high heats of absorption as shown in Table 6.

The reboiler duty required for stripping can be approximated as the sum of three terms: the heat required to desorb the CO₂, that required to generate the water vapor at the top of the column, and the sensible heat requirement

$$Q = Q_{\text{des}} + Q_{\text{H}_2\text{O gen.}} + Q_{\text{sens}} \tag{6}$$

$$= \Delta H_{\text{des}} + \left(\frac{n_{\text{H}_2\text{O}}}{n_{\text{CO}_2}} H_{\text{vap}}\right) + \left(\frac{L Cp \Delta T}{n_{\text{CO}_2}}\right)$$
(7)

Table 6 shows the contributions to the reboiler duty for $6.4 \text{m K}^+/1.6 \text{m PZ}$ and MEA/PZ. The major difference between the reboiler duties is the relative amount of the heat of desorption of CO_2 , and the heat required to generate the water vapor at the top of the stripper. It is more attractive to strip $6.4 \text{m K}^+/1.6 \text{m PZ}$ at 30 kPa than at 160 kPa. Normal pressure favors solvents with high heats of desorption, such as MEA/PZ.

Generic solvent modeling

A three-parameter expression for the vapor-liquid equilibrium was used to model generic solvents

$$\ln P = a + b^* \log \cdot \frac{\Delta H}{RT}$$
 (8)

The constant b, was set to 24.76, while the constant a, was varied. The value of the constant a, used in Eq. 8 for the generic solvents is shown in Table 7.

Figure 5 shows the minimum total equivalent work for the generic solvents at 160 kPa and 30 kPa with a 5°C approach on the hot side of the cross exchanger.

Table 7. Constant in Generic Solvent VLE Expression

$\Delta H_{\rm abs}$ (kJ/gmol CO ₂)	a
42	3.82
63	11.85
83	19.89
105	27.92
126	35.96
146	43.99
167	52.03

The results show that at 160 kPa, the optimum generic solvent is one with a heat of absorption of ~ 126 kJ/gmol CO₂ that is greater than 7m MEA (80–100 kJ/gmol CO₂).

At 30 kPa, the optimum generic solvent is one with a heat of absorption ~ 80 kJ/gmol CO₂ (about that of 7m MEA). For solvents with $\Delta H_{\rm abs} < 60$ kJ/gmol CO₂, stripping at 30 kPa is more attractive than stripping at 160 kPa.

Figure 6 shows the reboiler duty for the generic solvents at 160 kPa and 30 kPa. The reboiler duty is minimized at \sim 80 kJ/gmol CO₂ at 160 kPa and \sim 63 kJ/gmol CO₂ at 30 kPa. Figure 6 shows that for solvents with $\Delta H_{\rm abs} < 40$ kJ/gmol CO₂, stripping at 30 kPa may be more attractive than stripping at 160 kPa in operations where energy use is not critical, for example in natural gas processing.

Predicted Performance of Alternative Configurations. Table 5 shows that the multipressure configuration with a 160 kPa reboiler is more attractive for the solvents with a high heat of absorption than solvents with a lower heat of absorption. The performance of the alternative configurations is matrix > internal exchange > multipressure with split feed > flashing feed. The matrix and internal exchange configurations with a 160 kPa reboiler and 5 K approach with 7m MEA offer 9 and 11% energy savings, respectively, over the simple stripper operated at 160 kPa with a 5 K approach.

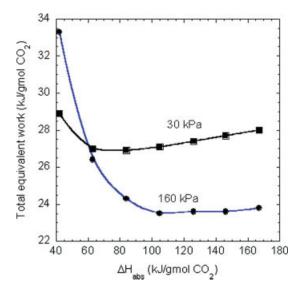


Figure 5. Total Equivalent Work for Generic Solvents (Rich $P_{\text{CO}_2}^* = 5$ kPa at 313 K, $\Delta T = 5$ K, 90% removal, $P_{\text{final}} = 1000$ kPa).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

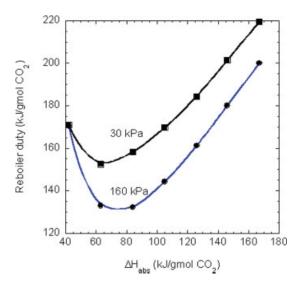


Figure 6. Reboiler duty for generic solvents (Rich $P_{CO_2}^*$ = 5 kPa at 313 K, ΔT = 5 K, 90% removal).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The characteristics of the matrix (265/160 kPa) and 160 kPa strippers for MEA are shown in Table 8. The matrix stripper recovers about 40% of the CO₂ at a higher pressure, and does not have the inefficiencies associated with the multipressure stripper. The reboiler duty is also slightly less for the matrix than the normal pressure stripper.

The characteristics of the vacuum, and the vacuum internal exchange strippers are in Table 9. The major difference between the two configurations is the difference in the ratio of the water vapor to CO_2 in the overhead stream. The internal exchange stripper has a smaller ratio of water vapor to CO_2 . Multipressure with split feed reduces the flow into the bottom section of the stripper, and, thus, equivalent work. The flashing feed makes use of the latent heat of water vapor in the simple/vacuum configuration to strip some CO_2 in the rich stream entering the stripper at the top of the column.

Solvent Performance. Table 5 shows the performance of the different solvent types. The results show that at 160 kPa, MEA/PZ, MDEA/PZ, and KS-1 require significantly less equivalent work than 7m MEA. MEA/PZ offers a 13 and 8% savings over 7m MEA with the matrix and internal exchange configurations at 160 kPa. MDEA/PZ was the most attractive solvent *in vacuo* conditions. MDEA/PZ offers a 14 and 10% savings over 7m MEA, with the matrix and internal

Table 8. Performance of Matrix (265/160 kPa) Stripper and Normal Pressure (160 kPa) for MEA (Rich loading = 0.563 mol CO₂/mol Alk, lean loading = 0.442 mol CO₂/mol Alk, $\Delta T = 5$ K, $P_{\rm final} = 330$ kPa)

	P	Fraction of CO ₂ removed	Q	$W_{\rm comp}$	Total $W_{\rm eq}$
	kPa			kJ/gmol C	202
Matrix	265	0.4	56	2.1	17.9
	160	0.6	58		
160 kPa	160	1	123	2.9	19.7

exchange configurations at 30 kPa. This shows that, at normal pressure, solvents with high heats of absorption and reasonable capacities are attractive. *In vacuo* conditions, solvents with lower heats of absorption and higher capacities are attractive. Capacity seems to play a more important role in determining energy requirements at vacuum conditions.

Effect of Heat of Absorption. From Table 5, solvents with similar capacities, but different heats of absorption can be compared. 6.4m K $^+$ /1.6m PZ and 5m K $^+$ /2.5m PZ are compared. The results show that at a fixed capacity, solvents with high heats of absorption require less energy for stripping. This is a consequence of the temperature swing. The 5m K $^+$ /2.5m PZ offers 18% savings over 6.4m K $^+$ /1.6m PZ at 160 kPa with a 5 K approach and savings of 3 and 4%, with the matrix and internal exchange configurations at vacuum conditions.

Effect of Capacity and Mass-Transfer Rates. The capacity of a solvent is defined as the amount of CO_2 a solvent can absorb over a given range of loading or partial pressure. This reflects the vapor-liquid equilibrium characteristics of a solvent. A high-capacity solvent can absorb or desorb more CO_2 than one with a low-capacity. Some solvents can also achieve richer loading because they have greater rates of CO_2 absorption.

In Table 5, 5m K $^+$ /2.5m PZ and MDEA/PZ have similar heats of absorption. However, MDEA/PZ has a greater capacity, and is also assumed to achieve greater equivalent rich loading than 5m K $^+$ /2.5m PZ. Therefore, MDEA/PZ provides 30 and 19% energy savings over 5m K $^+$ /2.5m PZ, with the matrix and internal exchange configurations with the reboiler operating at 160 kPa and 17 and 12% savings with these configurations at 30 kPa.

The two MEA solvents also have similar heats of absorption. MEA/PZ represented by 11.4 m MEA has a higher-capacity and rich loading than 7m MEA. MEA/PZ offers 13% energy savings over 7m MEA, with the matrix stripper operated with a 160 kPa reboiler temperature.

On the other hand, KS-1 is never quite as good as MDEA/PZ, even though it has a slightly greater heat of absorption and a slightly greater capacity. The primary difference in this case may be the rich $P_{\rm CO_2}$. Because it is assumed to be a slower reacting hindered amine, KS-1 was assigned a value of 5 kPa compared to 7.5 kPa for MDEA/PZ.

Insight into Stripper Operation. McCabe-Thiele plots provide insight into stripping phenomena. Figure 7 shows the McCabe-Thiele plot for 6.4m K⁺/1.6m PZ at 30 kPa comprising a flash section, 10 segments, and an equilibrium

Table 9. Characteristics of the Vacuum and Vacuum Internal Exchange Strippers for 7m MEA (Rich Loading = $0.563 \text{ mol CO}_2/\text{mol Alk}$, Lean Loading = $0.442 \text{ mol CO}_2/\text{mol Alk}$, $\Delta T = 5 \text{ K}$)

	Vacuum	Vacuum Internal Exchange
$\left(\frac{P_{\text{CO}_2}}{P_{\text{H}_2\text{O}}}\right)$ at rich end	0.81	1.31
$\Delta H_{\rm des}$ (kJ/gmol CO ₂)	73	72
$\left(\frac{n_{\text{H}_2\text{O}}}{n_{\text{CO}_2}}\right) H_{\text{vap}} \text{ (kJ/gmol CO}_2)$	54	34
$\left(\frac{L Cp \Delta T}{n_{\text{CO}_2}}\right)$ (kJ/gmol CO ₂)	30	30
Q (kJ/gmol CO ₂)	157	135

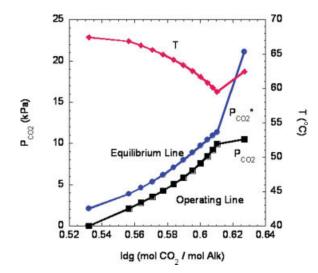


Figure 7. McCabe-Thiele plot for 30 kPa stripper using 6.4m K+/1.6m PZ with 10 segments (rich loading = 0.627 mol CO₂/mol Alk, lean loading = 0.532 mol CO₂/mol Alk, $\Delta T = 5$ K).

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reboiler. Since this column is not pinched, it could benefit significantly by using more contacting. This is shown in Figure 8, where the number of contacting segments is doubled. Flashing of the rich solution occurs at the top of the column. A rich end pinch is observed. The total equivalent work to generate CO₂ at 330 kPa increases from 23.7 kJ/gmol CO₂ with 10 segments to 23.2 kJ/gmol CO₂ (a 2% reduction) when the number of segments is doubled. Increasing the number of segments implies increased capital cost.

The McCabe-Thiele plot for 7m MEA with the matrix (265/ 160 kPa) configuration is shown in Figure 9. It is observed that

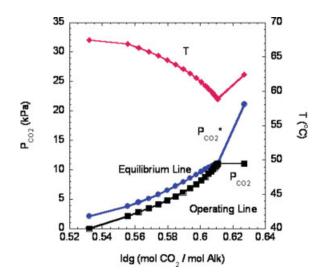


Figure 8. McCabe-Thiele plot for 30 kPa stripper using 6.4m K+/1.6m PZ with 22 segments (rich loading = 0.627 mol CO₂/mol Alk, lean loading = 0.532 mol CO₂/mol Alk, $\Delta T = 5$ K).

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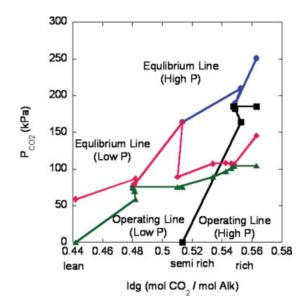


Figure 9. McCabe-Thiele plot for matrix (265/160 kPa) stripper using 7m MEA (rich loading = 0.563 mol CO₂/mol Alk, lean loading = 0.442 mol CO_2 /mol Alk, $\Delta T = 5$ K).

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the high-and low-pressure columns are highly pinched. A significant amount of CO2 desorption occurs due to flashing and under boiling conditions in the reboiler. The rich, semirich, and lean loadings are 0.563, 0.513, and 0.447 mol CO₂/mol Alk. This implies that a significant amount of desorption occurs in both sections of the low-pressure column.

Figure 10 shows the McCabe-Thiele plot for the internal exchange stripper with 7m MEA at 160 kPa. The feed is

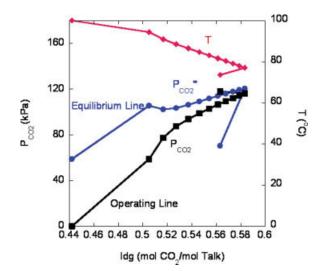


Figure 10. McCabe-Thiele plot for internal exchange stripper using 7m MEA at 160 kPa (rich loading = 0.563 mol CO₂/mol Alk, lean loading = 0.442 mol CO₂/mol Alk, $\Delta T = 5$ K).

[Color figure can be viewed in the online issue, which is available at www.interscience.wilev.com.l

Table 10. Energy Requirement for Separation and Compression to 10 MPa

	W_{sep}	W _{comp} to 330 kPa	$W_{\text{sep}} + W_{\text{comp}}$ to 330 kPa	W _{comp} (330 kPa to 10 MPa)	Total $W_{\rm eq}$		
Separation Method	kJ/gmol CO ₂						
Isothermal Sep. (313 K, 100 kPa), Ideal Comp. Isothermal Sep. (313 K, 100 kPa), 75% adiabatic	7.3	3.1	10.4	7.7	18.1		
compression in 5 stages	7.3	5.7	13.0	11.1	24.1		
Isothermal Sep. (313 K), 75% adiabatic compression							
in 5 stages (Membrane-like)	11.6	5.7	17.3	11.1	28.4		
Baseline (7m MEA, $\Delta T = 10 \text{ K}$, 160 kPa)	19.4	2.9	22.3	11.1	33.5		
Improved Baseline (7m MEA, $\Delta T = 5$ K, 160 kPa)	16.8	2.9	19.7	11.1	30.9		
Matrix 4m K ⁺ /4m PZ (295/160)	15.1	0.5	15.6	11.1	26.7		
Matrix MEA/PZ (295/160)	15.2	0.5	15.7	11.1	26.8		
Matrix MDEA/PZ (295/160)	14.6	0.5	15.1	11.1	26.2		
Matrix KS-1 (295/160)	15.6	0.5	16.1	11.1	27.2		
Matrix 4m K ⁺ /4m PZ (47/30)	9.6	8.5	18.1	11.1	29.1		
Matrix MEA/PZ (45/30)	10.7	8.7	19.4	11.1	30.5		
Matrix MDEA/PZ (45/30)	9.5	8.7	18.2	11.1	29.3		
Matrix KS-1 (45/30)	11.1	8.7	19.8	11.1	30.9		

subcooled with a loading of 0.563 mol CO₂/mol Alk. Some CO₂ absorption occurs at the stripper feed, increasing the loading to 0.583 mol CO₂/mol Alk in the first segment in the stripper before subsequent stripping. The stripper has a rich end pinch. A significant amount of stripping occurs in the reboiler, because it is assumed to be an equilibrium stage.

Effect on Power Plant Output and Process Improvement. The addition of an absorption/stripping system to a power plant will reduce the plant efficiency by reducing the net power produced from the plant, since steam is withdrawn from the plant to drive the reboiler and electrical power is used to operate compressors, blowers etc. Based on process analysis and economic studies, 35 the net power output of a 500 MW power plant is about 150 kJ/gmol CO₂ with 90% CO₂ removal. Different separation techniques are compared by separation and compression work in Table 10. The smaller energy requirements for fans and pumps have not been included in this analysis.

The total equivalent work for reversible isothermal separation to 100 kPa and 313 K, and subsequent compression to 10 MPa, is 18.1 kJ/gmol CO₂. This is the theoretical minimum work for separation and compression to 10 MPa. This constitutes about 12% of the power plant output. If reversible, isothermal separation to 100 kPA and 313 K is combined with a real, five-stage, intercooled compressor with 75% adiabatic efficiency, the total equivalent work is 24.1 kJ/gmol CO₂ (16% of the power plant output). If an isothermal separation, such as a perfect membrane is used to produce CO₂ at the partial pressure in the flue gas at 313 K, and its pressure is increased by a real five-stage, intercooled compressor with 75% adiabatic efficiency, the total equivalent work is 28.4 kJ/gmol CO₂.

The best solvent and process configuration is the matrix (295/160 kPa) with MDEA/PZ. This consumes 26.2 kJ/gmol CO_2 (18% of the net output from a 500 MW power plant with 90% CO_2 capture). This best case offers 22% energy savings over the current industrial baseline (7m MEA, $\Delta T = 10$ K, 160 kPa), and 15% savings over the improved baseline (7m MEA, $\Delta T = 5$ K, 160 kPa). This best case requires 2.1 kJ/gmol CO_2 more work than the theoretical minimum with real compressors. Because this analysis is attempting to account for the use of heat and work, it is sensitive to the

efficiency selected (75%) for the conversion of steam heat to work. Nevertheless, it appears that there is little room for improvement.

Conclusions

- 1. MEA/PZ and MDEA/PZ are solvent alternatives to 7m MEA that can reduce total equivalent work for the configurations studied.
- 2. The performance of the alternative configurations is matrix > internal exchange > multipressure with split feed > flashing feed.
- 3. At a fixed capacity, solvents with high heats of absorption require less energy for stripping. This is a consequence of the temperature swing effect.
- 4. Less energy is required with high capacity solvents with equivalent heat of absorption.
- 5. The typical predicted energy requirement for stripping and compression to 10 MPa (30 kJ/gmol CO₂) is about 20% of the power output from a 500 MW power plant with 90% CO₂ removal.
- 6. The best solvent and process configuration in this study, matrix (295/160 kPa) using MDEA/PZ, offers 22% energy savings over the baseline and 15% savings over the improved baseline with stripping and compression to 10 MPa.

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Notation

 ΔT = temperature approach in cross exchanger, K

 γ = CO₂ loading, mol CO₂/(mol MEA + mol K⁺ + mol 2 PZ + mol MDEA + mol KS-1)

Cp = heat capacity of liquid, kJ/mol-K

 $E_{\rm mv}$ = Murphree section efficiency defined in terms of partial pressures

 $g_{\rm CO_2}$ = mole rate of CO₂, gmoles/s

 ΔH = heat of absorption/desorption, kJ/gmol CO₂

 H_{vap} = heat of vaporization of water, 45 kJ/mol

 K_{CO_2} = equilibrium constant for CO₂, kPa L = liquid rate, gmoles/s

 $mol\ Alk = [mol\ MEA + mol\ K^+ + mol\ 2\ PZ\ + mol\ MDEA\ + mol$ KS-1]

 $n_{\text{CO}_2} = \text{mole of CO}_2$, moles

 $n_{\rm H,O}$ = mole of H₂O, moles

 P_{CO_2} = partial pressure of CO₂ in the bulk gas, kPa

 $P_{\text{CO}_2}^*$ = equilibrium partial pressure of CO₂, kPa P_n = partial pressures on sections n, kPa

 P_{n-1} = partial pressures sections n-1, kPa P_n^* = equilibrium partial pressure leaving section n, kPa

 $Q = \text{reboiler duty, kJ/gmol CO}_2$

 Q_{des} = heat of desorption of CO₂, kJ/gmol CO₂

 $Q_{\rm H_2O,gen}$ = heat of steam generation, kJ/gmol CO₂

 $Q_{\rm sens}$ = sensible heat required to heat rich solution to reboiler temperature, kJ/gmol CO2

R = universal gas constant, J/K-mol

T = temperature, K

 W_{comp} = isentropic work of compression, kJ/gmol CO₂

 $W_{\rm eq} =$ equivalent work, kJ/gmol CO₂

 $X_{\text{amine}}^{\text{o}} = \overline{\text{CO}}_2$ free amine mole fraction, mol amine/(mol amine + mol H₂O)

 $X_{\text{CO}_2} = \text{CO}_2$ liquid mole fraction, mol CO_2 /(mol amine + mol CO_2 + mol H₂O)

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