Distillation Absorption 2010
A.B. de Haan, H. Kooijman and A. Górak (Editors)

ENERGY EFFICIENT SYNTHESIS AND DESIGN FOR CARBON CAPTURE

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Abstract
Mononethanolamine (MEA)-based absorption-stripping for CO_2 capture is studied. Energy demands in this process are dominated by the stripping column. The shortest stripping line distance approach is used to determine minimum energy requirements for the MEA stripping column under various lean loadings. Simultaneous reaction and vapor-liquid equilibrium is assumed and modeled by the direct incorporation of experimental data. Results clearly show that the shortest stripping line distance approach easily determines minimum energy requirements and practical designs for the absorption-stripping process.

Keywords: MEA absorber-stripper processes, energy efficient design, shortest stripping line distance approach, data-driven simulation and optimization

1. Introduction

The rise in atmospheric carbon dioxide to levels approaching 400 ppm has spawned considerable renewed interest in capturing CO_2 from anthropogenic sources (e.g., power plants, transportation vehicles, etc.) in order to balance consumption of fossil fuels with environmental concerns. Carbon capture using monoethanolamine (MEA) and other amines (e.g., DMEA) in water is an old and well established technology[1,2] capable of achieving recoveries in the range from 80-90 mol% of CO_2 in power plant applications using solvent concentrations ranging from 20 to 30 wt% MEA in water. Unfortunately, carbon capture with MEA is energy intensive requiring approximately 30% of the energy produced in the power plant. The energy requirements of the MEA absorption-stripping process are dominated by the stripping column, which strips CO_2 from the solvent as an overhead vapor product and, in doing so, regenerates the solvent for recycle to the absorber. Little or no solvent is lost from the stripping column to the environment because of the high boiling point of MEA.

1.1 Absorber-Stripper Process Flowsheet and Feasible Design

Figure 1 shows a typical simplified process flowsheet for an MEA absorber-stripper process.

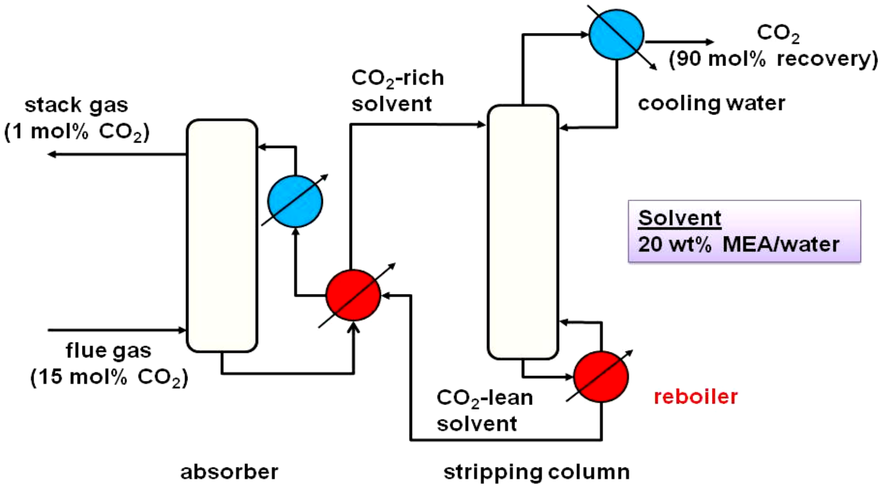


Figure 1. Monoethanolamine Absorber-Stripper Process for CO_2 Recovery

The focus of this study is the stripping column. Table 1 gives some typical design results for the stripping column using a 20 wt% solution of MEA in water for a CO_2-rich solvent loading equal to 0.5 mol CO_2/mol MEA (i.e., the saturated liquid feed to the stripper) and a bottoms stream or lean loading of 0.15. In this example, the stripping column pressure is 1.9812 bar, the boil-up ratio is s = 0.16500 and the partial condenser temperature is 30 C. Simultaneous phase and reaction equilibrium was assumed on all stages including the reboiler and partial condenser, which was computed directly from experimental data and will be described in more detail in section 1.2.

Table 1: Liquid Composition and Temperature Profiles for Stripping Column

	x_{CO2}	x_{water}	x_{MEA}	Temp (C)
Condenser	0.0001	0.99990	0	30
Stage 4	0.02763	0.91260	0.05977	101.79
Stage 3	0.01661	0.92362	0.05977	117.99
Stage 2	0.01249	0.92774	0.05977	120.58
Reboiler	0.01044	0.91994	0.06962	121.82

1.2 Vapor-Liquid Equilibrium

Phase behavior of CO_2-MEA-water mixtures is described by simultaneous phase and chemical reaction in the presence of carbonate, bicarbonate and hydrogen ions, making phase modeling challenging. Recent popular phase models[3] use the electrolyte non-random two-liquid (NRTL) equation fitted to data to model liquid behavior and assume ideal or non-ideal vapor behavior. Models of the separation equipment also vary – ranging from equilibrium models to rate-based models. Recently, Freguia and Rochelle[3] have demonstrated the use of RateFrac coupled with the electrolyte NRTL and Redlich-Kwong models in simulating CO_2 capture by MEA absorption and stripping.

1.3 Data-Driven VLE, Simulation and Optimization

In this work, the stripping column is modeled using an equilibrium stage model while phase behavior is modeled by directly using experimental partial pressure data for CO_2 over a 20 wt% solution of MEA in water[4] as well as experimental data for the partial pressure of MEA and water[4]. This means that liquid phase compositions (i.e., the solubility of CO_2 in 20 wt% MEA and water) were determined by interpolating a set of experimental data of temperatures ranging from 30 to 125 C and various liquid loadings of CO_2 in a 20 wt% solution of MEA in water ranging from 0.1 to 0.55. Specifically, we used a two-dimensional interpolation in temperature and CO_2 loading to determine liquid composition. That is, the CO_2 loading gives the number of moles of CO_2/mole of MEA. From this and the fact that the MEA solution is 20 wt%, it is straightforward to calculate liquid composition. As a result, no explicit liquid phase model is needed and the resulting VLE accounts for all non-idealities (i.e., reaction, the presence of ions, hydrogen bonding, etc.) in an implicit and efficient way. The vapor composition in equilibrium with the liquid composition on a given tray in the stripping column is computed by iteratively determining the stage temperature for which the sum of the partial pressures of CO_2, water and MEA equals the total system pressure. The partial pressures of CO_2 and MEA in the vapor phase were determined directly from experimental data given in Semenova et al.[4]. The partial pressure of water, p_{H2O}, was determined using the expression $p_{H2O} = P^{sat}(H_2O)x_{H2O}$ where the vapor pressure of water, $P^{sat}(H_2O)$, was determined from $\log_{10}[P^{sat}(H_2O)] = 8.14109 - 1810.94/(T + 244.485)$ where vapor pressure in mmHg and T is in C. Once the partial pressure of each component is known, the vapor composition for CO_2, MEA and water can be easily calculated from $y_i = p_i/p$, where p_i is a partial pressure and p is the fixed total pressure in the column. We reiterate the determination of any stage temperature is iterative.

2. Absorber Performance

Flue gas composition in coal-fired power plants is a function of coal composition. In this study, the specifications of the flue gas produced by a 600 MW hard coal power station were taken from Cifre et al.[5]. The flue gas feed to the process has a flow rate equal to $1.51\text{x}10^6$ nm^3/hr at a pressure of 1 bar and is 15 vol% CO_2. The goal is to remove 90% of the CO_2 from the feed stream. Following Semenova et al.[4], the maximum CO_2 loading of the rich solvent at the bottom of the absorber was assumed to be 0.5 mol CO_2/mol MEA while the loading of the lean solvent was assumed to vary from

0.15 to 0.25 mol CO_2)/mol MEA. The temperature of the lean solvent at the top of the absorber is 40 ^{0}C. In order to confirm the presence of finite driving forces measured by the difference between the partial pressure of CO_2 in the gas phase (p_{CO2}) and the equilibrium pressure of CO_2 over the solvent (p^*_{CO2}) along the absorber mass and energy balance equations have to be combined with the construction of equilibrium and operating lines. It is also known (Leites et al.[6]) that for a 20 wt% MEA solution the operating line approaches the equilibrium curve at the top and bottom of the absorber while the driving force at intermediate points of the absorption process is higher. This is due to the nature of the vapor-liquid equilibrium. This observation reduces the absorption process computations to that of checking the driving force at the top and the bottom of the absorber, which has to satisfy the condition $(p_{CO2} - p^*_{CO2})/p_{CO2} \geq 0.1$. The computations assuring this condition is satisfied involve trial and error calculations in temperature and MEA loading. Results of these calculations for different loading of the lean solvent are presented in Table 2.

Table 2: Specifications of the Absorber for Different Lean Solvent Loadings

Lean Loading	Rich Solvent Flow Rate (m^3/h)	Temp of Rich Solvent (C)
0.15	7888	49.7
0.17	8366	49.1
0.19	8906	48.5
0.21	9520	47.8
0.23	10225	47.2
0.25	11043	46.6

3. Minimum Energy Requirements and the Shortest Stripping Line Distance Approach

Lucia and co-workers[7,8,9] have recently shown that minimum energy requirements for a wide variety of distillation processes, including feed pinched, saddle pinched, tangent pinched, non-pinched distillations as well as multi-unit processes in which distillation is a part, can be readily determined using the concept of shortest stripping line distance. That is, minimum energy requirements for a given column correspond to the shortest stripping line distance from the bottoms product to the feed stage irrespective of whether the column is pinched or non-pinched, where the stripping line distance is measured by summing the quantities $||x_{j+1} - x_j||$ for j = 1, …, N_s where N_s is the number of stripping stages and || . || denotes the Euclidean two-norm. Thus the stripping line distance, $D(s, N_s)$, is a function of boil-up ratio, s, and number of stripping stages, N_s, and given by

$$D(s, N_s) = \sum_{j=1}^{N_s} ||x_{j+1} - x_j|| \qquad (1)$$

The quantity $x_{j+1} - x_j$ is determined using constant molar overflow stripping line equation

$$x_{j+1} - x_j = [(s)/(s+1)]y_j - x_j + [1/(s+1)]x_B \qquad (2)$$

where y_j is the vapor phase composition in equilibrium with the liquid composition x_j on stage j and x_B is the bottoms composition (lean solvent). Stages are numbered from bottom to top. Feasibility for the CO_2 stripper is a function of rich and lean loading and measured by satisfying distillate specifications. For the example, in the illustration given in Table 1, the target or specified overhead vapor needed to recover 90 mol% CO_2 from the flue gas and satisfy component mass balances around the stripper is $y_5(\text{spec}) = (y_{5,CO2}, y_{5,water}) = (0.5, 0.5)$. The illustrative separation is feasible if $||y_5(\text{spec}) - y_5(\text{calc})|| \leq 10^{-5}$ and, in general, if $||y_{Ns}(\text{spec}) - y_{Ns}(\text{calc})|| \leq 10^{-5}$.

In the shortest stripping line distance approach, optimization is used to find the minimum stripping line distance that gives a feasible separation. Specifically, $D(s, N_s)$ is minimized subject to Eq. 2 and the relationship between y_j and x_j for j = 1,…, N_s. In our feasible path formulation, the optimization variables consist of a single continuous variable, s, and a single discrete variable, N_s. We refer the reader to the papers by Lucia et al. for a detailed description of the shortest stripping line distance approach, which we use exclusively in this work to determine minimum energy requirements for a variety of CO_2 stripper configurations over a range of lean loadings.

3.1 Iterative Refinement

For stripping columns we use a bottom up approach to the design calculations. The basic idea behind iterative refinement for stripping columns comes from the fact that the specified and calculated distillate compositions rarely agree [i.e., y_{Ns}(spec) ≠ y_{Ns}(calc)] after one set of calculations from bottom to top. The same is true for general distillation columns and either the bottom up or top down approaches. Recently, Lucia and Hassan[10] have proposed a procedure based on Picard iteration for general distillation columns in which the distillate composition is iteratively refined until y_{Ns}(spec) = y_{Ns}(calc). See Lucia and Hassan[10]. For stripping columns, iterative refinement is simply given by

$$y^{k+1}_{Ns} = y^{k}_{Ns} \tag{3}$$

and only two iterations are required.

3.2 Minimum Energy Requirements for the CO_2 Stripping Column

Table 3 gives a snapshot of the determination of minimum energy requirements for a rich loading of 0.5, a lean loading of 0.15, and an overhead vapor target of $y_5 = (y_{5,CO2}, y_{5,water}) = (0.5, 0.5)$ using the shortest stripping line distance approach and iterative refinement. The column pressure was fixed at 1.9812 bar; there is no pressure drop within the column.

Table 3. Stripping Line Distance as a Function of Boil-up Ratio for a CO_2 Stripper*

Boil-up Ratio	No. of Stages	Distance
0.25650	3	0.14863
0.16500	4	0.10306
0.13020	5	0.08422
0.09430	9	0.06292
0.090958	10	0.06067

* rich loading = 0.5; lean loading = 0.15

Table 3 clearly shows that the stripping line distance decreases as the boil-up decreases and that the shortest stripping line distance approach easily determines the minimum energy requirements, which in this illustration correspond to a boil-up ratio of $s_{min} = 0.090958$. However, these feasible designs are very sensitive to the value of boil-up ratio and only exist within certain windows of boil-up ratio due to the strongly nonlinear phase behavior. The results in Table 3 also show that the minimum energy design is not pinched. That is, if an infinite number of stages are considered in an effort to reduce the boil-up ratio, there is a pinch point composition (i.e., a composition that remains unchanged as stages are added). However as the boil-up ratio is reduced, the corresponding pinch point compositions always yield a distillate product that fails to satisfy the overall component mass balances for the absorption-stripping process.

3.3 Condenser Considerations

The condenser can be simulated separately because the performance of the stripping column is 'independent' of the feeds (i.e., the rich solvent feed and the water reflux). Moreover, the amount of vapor leaving the top of the stripper is small in relation to the rich solvent feed and bottoms flow rates and contains essentially no MEA ($y_{MEA} < 10^{-4}$). Condenser operation can vary between 30 and 90 C. However, the phase split and flash calculations are easy, yielding almost a complete split (i.e., CO_2 with a little water to the vapor phase, water only to the liquid reflux phase). Table 4 shows the compositions of the feed to the condenser, the water reflux and the vapor distillate product for a partial condenser operated at 30 C and 1.9812 bar. The values of distillate-to-feed ratio (D/F) and reflux-to-feed ratio (R/F) for the condenser flash are 0.50833 and 0.49167 respectively. Phase split and flash calculations take very little time (0.06 s) using the terrain method of Lucia and Yang[11,12].

3.4 Feed Conditions & Water Reflux

The feed considered so far was a saturated liquid feed stream. However, in practice the rich solvent from the absorber exchanges heat with the lean solvent or bottoms stream from the stripping column.

Table 4. CO_2 Stripping Column Condenser Compositions

	Feed	Vapor Distillate	Water Reflux
CO_2	0.5	0.9835	0.0001
Water	0.5	0.0165	0.9999
MEA	0	0	0

See Freguia and Rochelle[3]. Thus the feed can be partially vaporized as it enters the stripping column. Partially or totally vaporized feed does not affect the stripping column design calculations but will increase the cooling requirements for the overhead condenser. In our opinion, it is much more important to avoid a sub-cooled feed stream from the absorber in order to avoid condensing vapor leaving the top tray because this will impact the recovery of CO_2 in the distillate product. Reflux ratios for the given designs range from 1 to 1.13. Moreover, since the reflux flow is very small (~0.01 of the feed) and should have little effect on the vapor flow leaving the top stage.

4. Minimum Energy Requirements for Various Lean Loadings

Table 5 gives minimum energy designs for various lean loadings ranging from 0.15 to 0.25 for a fixed rich loading of 0.5 moles CO_2/mole MEA where the specific reboiler duty is the sum of three terms – the heat of desorption of CO_2, the heat of vaporization of water, and the sensible heat required to raise the temperature of the rich loaded solvent to that of the bottoms product.

Table 5. CO_2 Stripping Column Minimum Energy Designs

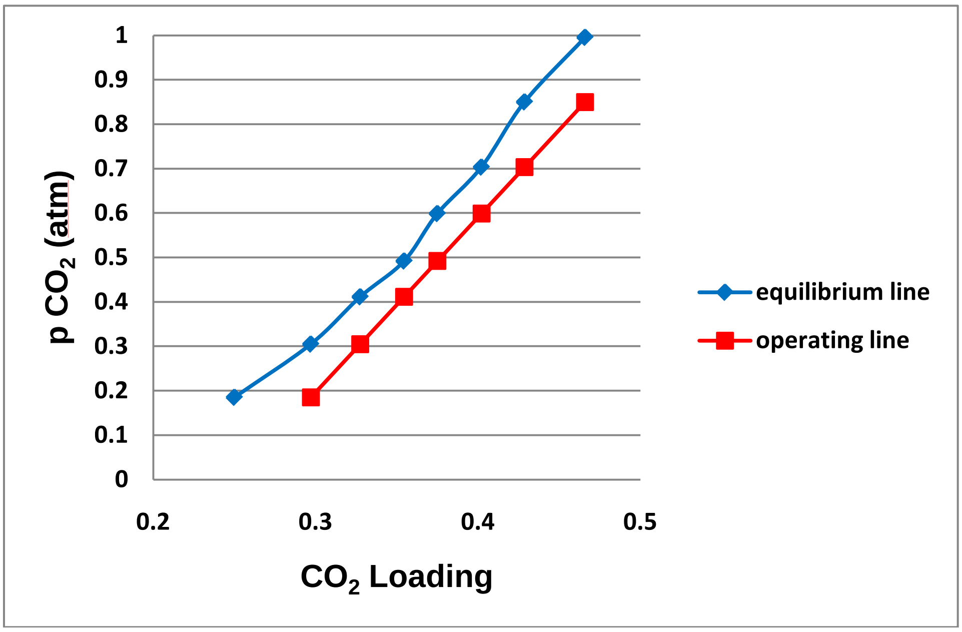
Lean Loading	Boil-up Ratio	D_{min}	No. of Stages	Specific Reboiler Duty (MJ/nm^3 CO_2)
0.15	0.090958	0.06067	10	11.4111
0.17	0.0733	0.04687	10	9.4980
0.19	0.0574	0.03737	10	8.2526
0.21	0.045999	0.02999	11	7.2357
0.23	0.0409	0.02592	8	6.6705
0.25	0.034129	0.02191	8	6.0724

All of the minimum energy designs are non-pinched minimum energy designs and each takes roughly 0.02 s to compute using our minimum stripping line distance software program on a Dell Core Duo pc using the Lahey-Fijitsu LF95 Fortran compiler and double precision arithmetic. This non-pinched nature of the designs is significant because it clearly shows the importance of the discrete variable, N_s, in the optimization.

In order to clearly illustrate that the designs in Table 5 are non-pinched, minimum energy designs, we have plotted the operating line (shown as lower/red line) and the equilibrium line (upper/blue) for a lean loading of 0.25 in the traditional manner for gas stripping operations – as a McCabe-Thiele diagram. Here the vapor composition is represented by the partial pressure of CO_2 and the liquid composition is given by the CO_2 loading. Note that the non-pinched nature of the minimum energy design is easily observed since the operating and equilibrium lines do not touch. We have also given the calculated temperature profile for the column, where the stages are number from bottom to top. The condenser is not shown in Figure 2.

5. Conclusions

Carbon capture using a 20 wt% MEA-water solution was studied. Vapor-liquid equilibrium was modeled by directly incorporating the experimental data of Semenova et al.[4] into the stripping column model, making our approach a data-driven approach to simulation. Numerical results show that minimum energy designs for CO_2 stripping columns can be correctly determined using the shortest stripping line distance approach of Lucia et al.[7,8,9] and iterative refinement[10]. These minimum energy designs differ from others presented in the open literature in that they are non-pinched and were validated by calculating the corresponding stripping pinch point and explained using simple overall mass balance concepts. Reboiler duties were computed and compare very favorably with literature values[6]. All solutions in this paper were also validated using the Aspen Plus simulator and the KEMEA model, which is available within the Aspen Plus modeling system.



Stage Number	T(C)
1	119.65
2	117.44
3	115.43
4	113.83
5	111.56
6	109.20
7	105.56
8	101.55

Figure 2. McCabe-Thiele Diagram for CO_2 Stripping Column

Acknowledgements

A. Lucia and A. Roy would like to thank the National Science Foundation for support of this work under Grant No. CTS-0624889.

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