Making Sense of Amine Absorber Temperature Profiles[1]

Ralph H. Weiland and Nathan A. Hatcher
Optimized Gas Treating, Inc.
112 Cimarron Park Loop, Suite A
Buda, TX 78610

Simulation is a powerful tool for ensuring designs are robust, operating conditions are optimal, and troubleshooting can be effectively and efficiently carried out. In gas treating applications for the removal of acid gases with amines, using the right simulation tool can make a critical difference. If the simulator used is truly mass transfer rate-based, an extremely useful simulation result is detailed profiles of temperatures, compositions, flows, and phase properties of the individual phases on each and every tray or incremental height of packed bed. Such profiles reveal potential design flaws or operating bottlenecks. Absorbers are commonly graced by temperature profiles showing sometimes quite high bulge temperatures located somewhere between the top and bottom of the column. The question being addressed in this article is not so much how high the peak temperature should be, but rather where in the absorber it should be located, and what controls this location.

Conventional wisdom seems to be that in amine absorbers the temperature bulge should always be near the bottom of the column—if it's not, something is wrong and the design may not be a good one. However, such a blanket statement can be quite misleading. The temperature bulge may be unavoidably at the bottom, the top, or the middle of the column even in an excellent design. Where it ends up is driven by treating objectives and depends primarily on the thermal properties of the phases being contacted and their relative flow rates. Of course the flow rates of the gas and liquid depend on the acid gas concentrations in the feed gas and the treating objective, as well as the particular amine in terms of its reactivity with carbon dioxide.

Case Studies

The impetus for this study is a question that arose during the design of an absorber to remove a relatively low concentration of mostly carbon dioxide using 2-(2-aminoethoxy)ethanol, known commercially as DIGLYCOLAMINE (DGA®) and amino-di-ethylene-glycol (ADEG®). The design was for treating just over 60 MMscfd of gas at 700 psig containing 0.9 mol% CO_2 and about 20 ppmv H_2S. Carbon dioxide is so aggressively absorbed by this amine that the rich solvent CO_2 loading could be kept below its recommended maximum only by using a lot more solvent than strictly necessary for carbon dioxide absorption. Figure 1 shows how the solvent temperature is simulated to change across the absorber using the ProTreat® simulator. Figure 2 shows the CO_2 loading profile.

Figure 1 clearly shows that most of the carbon dioxide is absorbed in the bottom half of the contactor. This suggests most of the heat is generated there, too. The question then is, if most of the heat of absorption is generated there, why is it that the lower half is not hot and the top half not cold? The explanation lies in the fact that each of the two flowing phases conveys the produced heat of absorption in its direction of flow. The gas phase conveys some of the heat

---

towards the top of the column, and the liquid phase conveys some towards the bottom. The phase that conveys the most heat determines the *position* of the bulge. The size of the bulge is determined by absorption rate and the heat of absorption. Thus, one must look at the mass flow rates of the gas and liquid, and their heat capacities. In this particular case, the liquid and gas heat capacities differ by only 30–40%. But the gas to liquid mass flow ratio is nearly four to one. This means that for a given temperature change, the gas carries roughly four times as much heat upward as the liquid carries downward. Thus, most of the heat of absorption is carried up the column, sweeping the heat released by absorption upwards, and making temperatures quite high beyond the location where most of the actual absorption and heat release take place. Of course, temperatures return to lower values at each end of the column because a colder gas or colder solvent is introduced there, driving temperatures down.
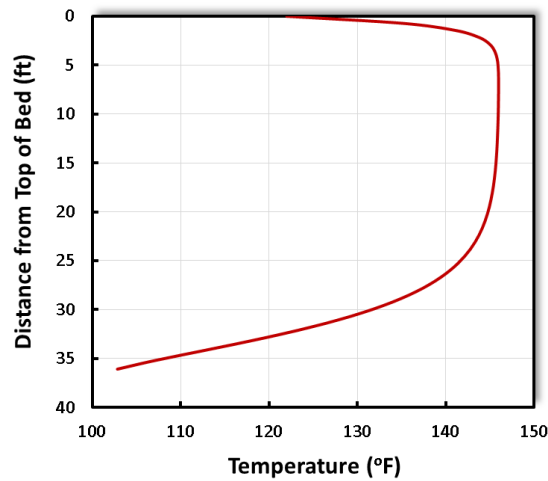
Figure 1   Absorber   Solvent   Temperature Profile using DGA/ADEG Solvent
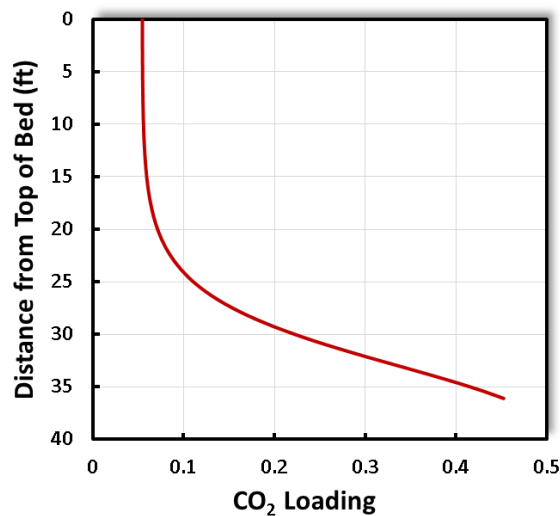
Figure 2   CO$_2$ Loading Profile across Absorber when using DGA/ADEG Solvent

The location of a temperature bulge and even the shape of temperature profiles is an interesting function of the L/G ratio in the absorber. To examine this further, both DGA/ADEG at 50 wt% and the nonproprietary solvent MEA at 30 wt% are used as the simulation basis. In both cases, the absorber is packed with #1.5 Nutter Rings. The CO_2 concentration is varied but the total molar flow rate of CO_2 is kept constant by adjusting the total gas flow rate. Since almost all the CO_2 in the feed gas is absorbed, keeping the total CO_2 flow constant means the total heat released by absorption remains the same from case to case. In all cases the absorber was simulated at 70% flood.

A Determining Factor

The ability of a phase to transport heat is the product of its heat capacity and its flow rate. Which phase dominates in conveying heat can be measured by the ratio of the inherent ability of the two phases; in other words, by what might be called the Heat Transport Capacity Ratio defined as:

$$HTCR = c_p^{(L)}L/c_p^{(V)}V$$

Here c_p is the mass or molar heat capacity, and L and V are mass or molar flow rates of liquid and vapour, respectively. Figure 3 shows how temperature profiles change with the value of HTCR for the DGA/ADEG solvent. Figure 4 shows similar results for 30 wt% MEA. Apart from piperazine-promoted MDEA (which shows similar profiles to Figures 3 and 4), the other amines do not react fast enough with CO_2 to allow such simple analysis to be used—the total of absorption rate of CO_2 cannot be kept constant without also adjusting the packing depth.
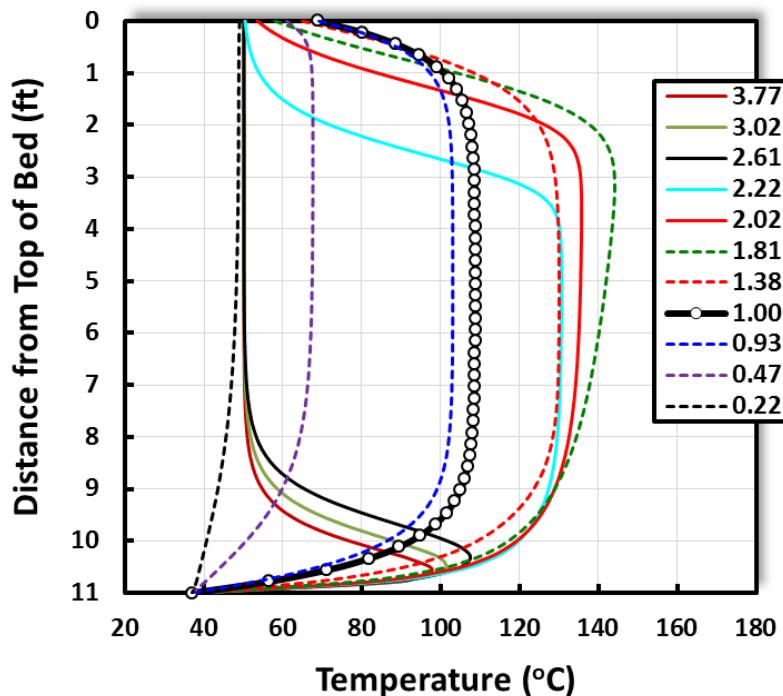
Figure 3   **How Absorber Temperature Profiles Change with Heat Transfer Capacity Ratio – CO_2 Absorption by 50 wt% DGA/ADEG. Legend Shows Value of HTCR.**
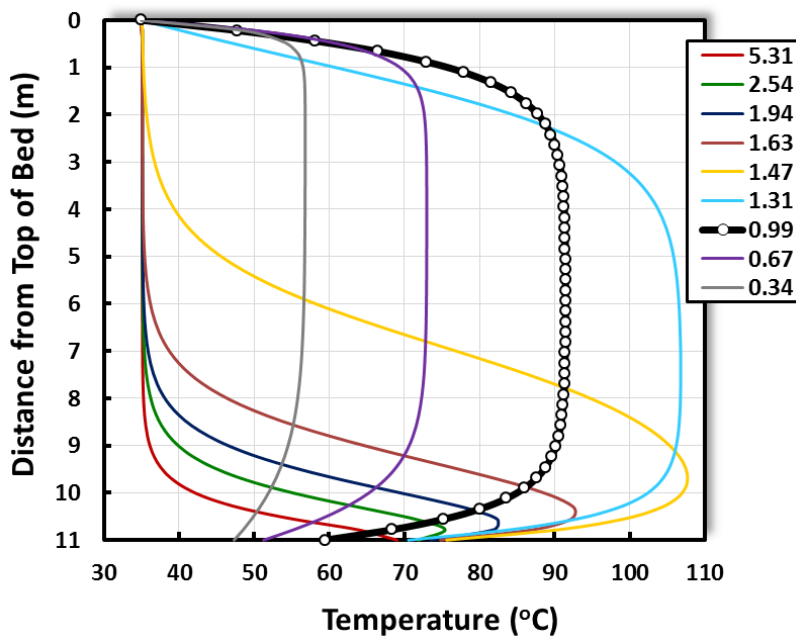
**Figure 4   How Absorber Temperature Profiles Change
with Heat Transfer Capacity Ratio – CO$_2$
Absorption by 30 wt% MEA. Legend Shows
Value of HTCR.**

A critical scan of these plots reveals there are three cases of interest: HTCR > 1, HTCR < 1 and HTCR ≅ 1. These correspond to heat flow with the liquid phase dominating, heat flow via the vapour phase dominating, and similar flow rates of heat via the vapour and liquid phases.

Regardless of the value of the HTCR, most of the absorption takes place in the lower half of the packed bed so most of the heat of absorption is released there. Phase flow rates determine how that heat is moved up and down the column, how it is spread out or held within the column's height and therefore, how high the bulge temperature actually becomes. It also determines where the bulge is located.

High Liquid Flow (HTCR > 1)

As the value of HTCR increases above unity, the operation becomes increasingly a high-liquid-rate one, in which case liquid flow rate dominates and the bulk of the heat of absorption is carried predominantly out the bottom of the column. This results in the well-recognised bottom bulged temperature profiles that, *mistakenly*, many would call the only normally expected, shape. At the highest liquid rate (HTCR value of 5.31) the temperature bulge is sharp, steep, and pushed right against the tower bottom. The liquid flow rate increases, temperature rise does not have the opportunity to increase above about 67°C before the heat is carried away and leaves from the column bottom.

High Vapour Flow (HTCR < 1)

As the value of HTCR decreases away from unity (i.e., *vapor rate* increases), the temperature bulge itself *spreads* across more and more the column. At the same time its magnitude weakens. It spreads because heat generation is greatest near the bottom of the column and the heat is immediately picked up by the vapour. There is nowhere else for it to go except to continue upwards and out the top. The vapour is necessarily cooled right adjacent to the top of the column because it meets a cooling stream of solvent there; that's why it drops at the top of the column. Further increases in vapour rate make the temperatures even lower and drive the bulge against the top of the absorber. The *magnitude* of the bulge decreases with increasing vapour flow because the heat of reaction is diluted by an ever larger vapour flow. In short, at high flow rate, the gas does not have to become nearly as hot to remove the heat of absorption.

Neither Phase Dominates (HTCR $\cong$ 1)

Starting from the high HTCR end of the range, increasing vapor rates result in still higher temperatures. More and more of the tower is hot. At a value of 1.31 (MEA case) the bulge is very hot indeed, and it occupies the lower 2/3-rds of the packed bed. When the ratio reaches a value of roughly unity, however, the profile becomes symmetrical about the mid-level of the column. The vapor and liquid are now transporting roughly an equal portion of the reaction heat from the column.

As gas rate increases the temperatures first become very high because the rising vapor in the top of the column transfers a lot of its heat to the cool descending liquid. At the same time, the hot falling liquid gives up a lot of its heat to the cold rising vapor in the bottom. Each phase carries roughly an equal amount of heat back and forth, up and down the column. The heat of absorption can get trapped in the central region; hence, temperatures there can become extremely high. In other words, although the liquid is still carrying heat out the tower bottom, that heat flow is being countered by vapor picking up heat from the liquid and carrying it upwards. Likewise, heat carried upwards by the vapor gets released back into the liquid before being carried out the bottom. When HTCR is about unity, profiles are roughly symmetrical; any asymmetry results from differences between inlet gas and liquid temperature, and not from flow conditions in the column. The transition from bottom to top bulges occurs at the point of symmetry, i.e., when the HTCR is about unity.

Conclusion

The exact shape of the temperature profile as well as the bulge position and its value depend on the chemical system and the operating conditions of the absorber. Sometimes even a rather sharp upper-end bulge is evident. The purpose here is to point out that seeing "unusual" temperature profiles is quite normal in mass transfer rate-based simulation, and in real operating columns. All the temperature profiles generated by true mass transfer rate-based simulation have rational explanations. There are also ways to move temperature profiles and bulges around by judiciously selecting the right operating conditions (including the tower internals).

The wide range of temperature profiles and bulge locations shown here result from situations ranging from removing a high CO_2 concentration from a low flow rate gas stream, to CO_2 removal from a low concentration, high flow rate gas. The total amount of CO_2 removed being the same across all cases, these extreme processing conditions result in very high and very

low L/G ratios, and the attendant temperature profiles are quite disparate. There is no "standard" or "right" temperature profile. They vary widely!

The maximum advised temperature anywhere in an amine absorber is roughly 85°C, at least with carbon steel metallurgy. As these case studies show, much higher temperatures can be reached under many different conditions. The important fact though, is that every case displayed in Figures 3 and 4 results in (1) reasonable exit stream temperatures from the absorber, and (2) absorber performance that meets a low residual CO_2 treating objective (parts per million). In the present cases, most simulators will produce similar *overall* results for a *standalone* absorber in terms of outlet stream conditions and level of treating simply. This is because overall CO_2 removal is determined in this case by lean loading, i.e., regenerator performance. Ultimately, lean loading is the result of the mass transfer rate processes occurring in the regenerator— regenerators must be simulated using a real mass transfer rate model, too.

In the cases discussed here, if just meeting overall treating goals were the only objective, superficially any one simulator would do as well as any other—these absorbers are lean pinched and lean loading completely determines treating. However, if mass transfer rates control performance, then anyone using a simulator other than one based on true mass transfer rates must have a very good handle on HETP values and how they change with packing type and size, and with fluid properties and flow rates. Such a database simply does not exist; consequently, the designer who uses ideal stage-based models *of any kind* no matter how the model is embellished is left to guess and hope, not a great basis for a design. Furthermore, if keeping temperatures low enough to maintain tower shell integrity against rapid corrosion is important, for example, getting an accurately detailed picture of internal temperatures (and solvent loading) is important. This cannot be achieved with certainty without a fully mass transfer rate-based simulation tool such as ProTreat®.