Factors Influencing the Location and Magnitude of Temperature Bulges in Amine Contactors

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Introduction

Knowledge about the behavior of temperature bulges in amine systems is of considerable importance, especially if instrumentation does not allow the bulge to be directly monitored. A high temperature bulge can create corrosion or degradation issues while the unit otherwise performs as intended. As instrumentation often does not allow direct monitoring of the temperature bulge, the operator is left blind to the presence of a high temperature bulge, and the negative effects are allowed to continue longer than normally would be the case.

Previous works examined the impact of liquid-to-vapor feed rate ratios on the location and magnitude of temperature bulges in amine absorbers. In 2008, Kvamsdal and Rochelle [1] investigated the impact that varying liquid-to-vapor ratio has on the maximum temperature bulge for MEA systems. That work investigated a *molar* ratio and compared simulated results to pilot scale data. Weiland and Hatcher [2] considered the mass flow and heat capacity of each phase, not just the molar ratios. That work provides a thorough discussion of heat recycle in amine absorbers where a lean-end pinch was expected. A critical ratio was shown where a "maximum T-bulge" is achieved due to heat recycle in the column as the ratio of the product of mass flow and heat capacity for each phase approaches unity.

This work continues the course of considering ratios of thermal masses, here termed Thermal Mass Ratio (TMR), with the additional consideration of systems where rich pinches are either expected or approached. Thermal mass ratio is defined as the product of the mass flow and heat capacity of the liquid, divided by the product of the mass flow and heat capacity of the vapor, denoted as:

$$TMR = \frac{\dot{m}_L * C_{p,L}}{\dot{m}_V * C_{p,V}}$$

In general, system designers desire or expect a "pot belly" temperature profile where the maximum temperature and the highest driving forces occur in the bottom third of the column. Figure 1 shows an example of this temperature profile from a ProMax[®] [3] simulation. All further figures are results from the simulator unless otherwise noted. Figure 2 shows the partial pressure of acid gas each of the phases for this "potbelly" system, providing an indication of driving force.



Figure 1: Typical "Potbelly" Absorber Temperature Profile



Figure 2: Driving Force Profile for "Potbelly" Conditions

A system like what is shown produces a relatively low maximum temperature and sufficient driving force at the bottom for bulk removal. The warm rich amine carries most of the heat of reaction out the bottom of the column with little opportunity for heat recycle to the vapor. However, the bulge can move up or expand through changes to the TMR. The location and magnitude of this bulge is especially sensitive in areas where the solvent becomes loaded, and the partial pressure of acid gas in the liquid approaches that of the vapor. This results in a lack of driving force at the bottom of the column, commonly referred to as a rich-end pinch.

As noted by Weiland and Hatcher, for a given system, as TMR decreases the heat carrying capacity of the liquid decreases relative to the vapor. As a result, heat moves up the column where, once TMR decreases enough, it can leave the system in the overhead sweet gas. As TMR increases, the reverse is true. The relative heat carrying capacity of the liquid increases, and heat tends to be carried towards the bottom where, once TMR increases enough, the heat leaves the system in the rich amine. It has been posited that TMRs of unity lead to the highest amount of heat recycle and subsequently the maximum bulge temperatures. If one considers the column an analog of a heat exchanger, this should be entirely true.

However, there are additional considerations beyond pure heat exchange that can affect the magnitude of the temperature bulge, such as the location and magnitude of heats of reactions in different parts of the column. For a given acid gas concentration and solvent strength, there is a TMR that provides the highest bulge temperature. This TMR may not be at or near unity. However, if considering the universe of various combinations of acid gas concentration and solvent strength, the system that shows the *highest bulge temperature of all systems* does so when the TMR is close to one. This will be shown in a following section.

TMR and Driving Force

Figure 3 shows an example MDEA/Piperazine system where the impact of TMR and driving force on the size and location of the temperature bulge can be seen:



Figure 3: Example Acid Gas Absorber and Conditions

The base system is a 45/5 wt% MDEA/Piperazine blend treating a sour gas containing 3.5 mol% CO₂ at the given conditions. For this system, a lean flow rate of 420 sgpm equates to a TMR of approximately 1.25. This system has a driving force pinch in the middle-to-bottom section of the column. This pinch reduces mass transfer, but heat transfer is unimpeded and the bottom trays behave as a series of heat exchangers. Figure 4 shows a driving force profile of this system.



Figure 4: Driving Force Profile for Example Absorber with TMR=1.25

Holding all other conditions constant, a circulation rate of 340 sgpm, gives a TMR of 1, and 505 sgpm, gives a TMR of 1.5. As can be seen in Figure 5, the highest temperature bulge occurs when a rich pinch condition and a particular TMR squeezes the bulge to the middle of the column. For this case, the highest bulge did not occur at a TMR of unity.



Figure 5: Temperature Profiles for Example Absorber at Various Thermal Mass Ratios

In the TMR 1 case, the vapors leave the system warmer (149 °F), allowing heat to leave the column with the sweet vapor. This reduces the magnitude of the bulge even though a rich pinch condition persists. For the TMR of 1.5, the rich amine leaves warmer (145 °F), a result of the absence of a rich pinch and movement of heat generation to the bottom of the column. The driving force for this TMR 1.5 case is the system shown in Figure 2.

In the end, the rich pinch condition moves heat generation up the column and allows the vapor the opportunity to strip heat from the descending liquid, which increases the bulge temperature in the middle of the column. When this occurs, the driving force collapses further and acid gas pick up spreads over the entirety of the column as opposed to the bottom section. When a rich pinch is approached and the TMR is such that the bulge is near the middle of the column, a maximum bulge temperature occurs. Driving force and TMR compound each other in this manner.

To illustrate how the heat transfer at the bottom of the column affects the temperature bulge as well as the driving force, the low bulge TMR 1.5 system is modified in Figure 6. The rich amine preheats the feed gas such that the rich amine and sweet gas leave at a temperature of 135 °F, the same conditions as the TMR 1.25 case. This approximates the heat recycle that the TMR 1.25 case experiences. Figure 7 and Figure 8 represent the resultant driving force and temperature profiles, respectively.



Figure 6: Example Absorber with Forced Heat Recycle via Gas/Liquid Heat Exchanger



Figure 7: Driving Force Profile for Example Absorber with TMR=1.5 and Forced Heat Recycle



Figure 8: Comparison of Example Absorber Temperature Profiles at Different Conditions

As can be seen, the heat recycle collapses the driving force, creating a rich pinch that did not exist before. This shifts the heat of reaction upwards, and the heat recycled in the bottom sections of the column push the bulge to a high maximum, similar to the TMR 1.25 system. If the solvent strength increases or the acid gas concentration of the feed decreases, this high temperature bulge would contract, as the system would move away from pinch conditions. This concept will be explored further in the next section.

Simulation Study Background

A simulation study investigated how solvent concentration and TMR affect absorber peak temperatures. The study used the following parameters:

- 100 °F and 1000 psig feed gas and lean amine temperature and pressure
- Feed gas composition (mol%): N₂-2.5, C₁-72.6, C₂-13.3, C₃-7.3, iC₄-0.73, nC₄-2.25, iC₅-0.5, nC₅-0.47, nC₆-0.35; with CO₂ displacing C₁ to study different CO₂ concentrations
- Fixed feed gas flowrate of 10,000 lbmol/hr
- Defined lean amine mixture of water, MDEA, piperazine, and CO₂ only
- 9:1 mass ratio of MDEA:piperazine
- Fixed lean loading of 0.025 mol CO₂/mol amine
- Solvent flowrate varied to adjust TMR
- Column diameter fixed at 90 in, which resulted in flooding ranging from 40-50%
- 20 single-pass trays in column with 3 in weirs and 70% active area

Is there a peak at TMR = 1?

Figure 9 shows the absorber peak temperature versus TMR with a 2.5 mol% feed gas CO_2 and solvent concentrations from 20-60 wt% amine. When the solvent flowrate is varied to adjust the TMR, a maximum temperature peak exists for each solvent concentration. Besides the existence of these local maximums, there are two other behaviors of note. First, the maximum of all maximum peak temperatures resides near TMR = 1. Second, the shape of the concentration curves changes as the solvent concentration changes. The lower concentration curves, corresponding to points where TMR>1, rise to sharp maximum temperature peaks, while the higher concentration curves, corresponding to points where TMR < 1, rise and fall more gradually.



Figure 9: Absorber Peak Temperatures for MDEA/PZ System at Various Solvent Strengths and 2.5% CO2 in Feed Gas

These two behaviors do not appear to be unique to the system in Figure 9. Figure 10 and Figure 11 show this same behavior for a 3.5 mol% CO_2 system with MDEA/PZ and a 2.5 mol% system with DGA[®] [4], respectively.



Figure 10: Absorber Peak Temperatures for MDEA/PZ System at Various Solvent Strengths and 3.5% CO2 in Feed Gas



Figure 11: Absorber Peak Temperatures for DGA System at Various Solvent Strengths and 2.5% CO2 in Feed Gas

As stated previously, the maximum bulge temperature is expected where TMR is close to one. That the maximum of all maximum temperatures occurs with a TMR near one in Figure 9-Figure 11 seems to confirm this logic. However, that the maximum temperature for a given solvent concentration does not necessarily correspond to or gravitate towards a TMR of one suggests that other factors have influence as well.

Does the Location of Heat Input Matter?

One factor that influences the location and magnitude of the temperature bulge is the location of heat generation into the system, as shown in Figure 12. In the simulation for this figure, a water-saturated, 1000-psig nitrogen stream enters the bottom of a 20-tray column and a nitrogen-saturated, 1000-psig 45/5 wt% MDEA/PZ solution enters the top. Flows are set to hold the TMR at unity. Each profile in Figure 12 represents the same total amount of heat added at different locations in the tower to mimic the effect of CO_2 absorption in different locations (nitrogen being inert, there is no heat of reaction).



Figure 12: Absorber Temperature Profiles for Non-Reactive System with Various Locations of Heat Input

The maximum bulge temperature occurs when heat addition moves from the bottom of the column to the middle, similar to what occurs in a column approaching a rich pinch. When heat generation occurs in the middle of the column as opposed to the bottom, the rising vapor can strip more heat from the liquid before the liquid exits the bottom of the column. This recycles heat back to the generation zone. When heat is added high in the column, the vapor exits the system at a higher temperature, carrying the heat with it and reduces heat recycle to the descending liquid. This pattern of heat leaving the system at a particular location depending on where it is absorbed holds regardless of the TMR, but a TMR at unity produces the highest temperature bulges.

Does the Magnitude of the Heat Input Change?

In addition to the location of heat input to the system, the magnitude of the heat input has an effect on the bulge temperature. An obvious cause for changes in the magnitude of the heats of reaction is the amount of CO_2 that is absorbed in the solvent on a given tray. For some systems, conditions may exist where a complete rich-pinch occurs and CO_2 begins slipping through the column overheads. This would result in reduced total heats of reaction. In addition, heats of reaction per mole are a function of solvent loading, going down as loading increases [5]. However, the change of the heat of reaction for typical solvent strengths is relatively small.

What gives each Solvent Concentration Curve a Maximum Value but Different Shape?

Given that the location and magnitude of heat input to a system affects the location and magnitude of the bulge, the question remains as to why the shape of each solvent concentration curve varies. To study the causes of these various shapes, three solvent concentrations were chosen from Figure 9. These selections are indicated in Table 1.

Solvent Strength	TMR	Maximum T
20wt%	>1	165F
35wt%	~1	192F
55wt%	<1	175F

Table 1: Selected MDEA/PZ Strengths for Study

Heat Input Location

Figures 13-15 show the CO₂-absorption per tray for each system at three different TMRs. The resultant temperature profiles are also provided. The TMR that exhibited the maximum temperature for each system is, as well as a TMR above and below this maximum bulge condition.



Figure 13: Absorption rate and temperature profile for 20% solvent concentration



Figure 14: Absorption rate and temperature profile for 35% solvent concentration



Figure 15: Absorption rate and temperature profile for 55% solvent concentration

Figure 13 shows that at 20 wt% solvent concentration, the bulk of the CO₂ absorption occurs in the middle of the column for the maximum-temperature TMR curve. This indicates a column approaching a rich-end pinch. The absorption zone moves down for higher TMR (higher solvent

flow), and moves up for lower TMR (lower solvent flow). As the solvent is already highly loaded and quickly approaches pinch conditions, it is quite sensitive to small changes in solvent flow.

For the 35 wt% solvent concentration shown in Figure 14, which gives the highest maximum peak temperatures, rich-end pinch and TMR appear to compete to determine where the maximum is located. When the TMR is above unity, the bulk of the heat generation occurs very near the bottom of the column. Decreasing TMR toward unity increases rich loading and moves heat generation up the column, but a considerable amount of heat generation remains near the bottom. The maximum temperature does not occur until the TMR moves slightly below unity. At this point, heat generation has moved toward the middle of the column, and the TMR is still close enough to unity to give efficient heat recycle.

For the 55 wt% solvent concentration shown in Figure 15, heat generation does move slightly upward as TMR decreases. This initially increases the maximum temperature before poorer heat recycle with lower TMR takes over.

Acid Gas Breakthrough Reduces Heat Input for Low Concentrations

Figure 16 takes the 20 wt%, 35 wt%, and 55 wt% curves from Figure 9 and overlays the sweet gas CO₂ concentration for each system, indicating where acid gas breakthrough may occur. The points corresponding to the TMRs used in Figures 13-15 are bolded.



Figure 16: Peak Temperature and Acid Gas Concentration in Sweet Gas for the Studied Systems

As pointed out previously, if acid gas breakthrough occurs, the overall amount of heat input to the system decreases. If one starts on the high-TMR side of the 20 wt% curves in Figure 16, and then begins to move to lower TMRs, the temperature rapidly increases until CO₂ starts to break through the top of the column. Once CO₂ breakthrough occurs, the temperature begins to decrease. Two mechanisms are cooperating to cause the rapid temperature rise on the right side of the 20 wt% curve. First, as the TMR decreases toward unity, heat recycle efficiency in the column improves.

Second, as the absorption zone and heat generation moves to the middle of the column, the opportunity for heat recycle up from the bottom trays improves.

For the 35 wt% case, acid gas breakthrough begins at a slightly lower TMR than what produces the peak bulge temperature. The rate of this breakthrough is significantly less than the 20 wt% case.

For the 55 w% case, there was no apparent acid gas breakthrough at any of the selected TMRs, so the heat input was essentially constant throughout the conditions studied.

Bringing it all together

In the range of TMRs selected, competing effects result in a rise, peak, and fall of the maximum bulge temperature in different ways for each of the solvent strengths.

20 wt% Case:

On the high TMR side, the loadings are the lowest, and the heat generation occurs in the bottom third of the column. The column removes all the acid gas, which maximizes heat input However, with heat input low in the column and a relatively high liquid thermal mass, the system has little ability to recycle heat back towards the center. Much of the reaction heat leaves in the rich amine.

As TMR is lowered, the magnitude of the heat input remains the same, but it begins to shift upwards in the column as loading increases and a rich-pinch is approached. This upward shift provides improved opportunity to recycle heat. This couples with a move in TMR towards unity, which increases the heat recycle efficiency. These effects compound, pushing the heat towards the center of the column and increasing the magnitude of the temperature bulge.

Eventually, as TMR decreases further, a full rich-pinch occurs. Acid gas breakthrough reduces the heat input, and the location of the heat input continues to shift upwards. This upward shift in heat input and a reduced TMR allows heat to begin to escape with the sweet gas. A sharp decline in the maximum temperature begins, primarily due to the increase in acid gas breakthrough.

35 wt% Case

On the high TMR side, as with the 20 wt% case, loadings are at their lowest, and heat generation occurs in the bottom third of the column. All of the acid gas is being removed, so the magnitude of the heat inputs is at its highest. With heat input lower in the column at high TMR, the opportunity for recycle diminishes. The higher TMR also pushes heat downwards, allowing it to exit in the rich amine.

As TMR decreases, loadings gradually increase, causing the location of heat input to shift up the column. A maximum bulge temperature occurs at a TMR just below unity. At this point, most of the heat input spreads over the middle to bottom half of the column, and a TMR near unity improves heat recycle efficiency. These effects combine to concentrate heat towards, but slightly below, the middle of the column, creating the maximum peak.

As TMR decreases further, a rich-pinch condition is approached. Some acid gas breakthrough begins, reducing the magnitude of heat input. The rich pinch shifts heat input upward, and the lower TMR decreases heat recycle back down the column. These two effects combine to help heat leave in the sweet gas as opposed to concentrating in the middle, and thus reduces the maximum

bulge temperature. As a full rich-pinch has not yet occurred, this decline shows some curvature rather than the straight line seen in the 20 wt% case.

55 w% Case

Owing to the relatively high solvent strength, the maximum temperature changes for this system are flat as compared to the lower solvent concentration systems. Loadings are low for all the TMRs in this system, and none of the TMRs approach a rich-pinch. The result is heat input to the bottom of the column for all TMRs studied. There is little in the way of acid gas breakthrough, so the magnitude of heat input is more or less constant. With much of the heat leaving the bottom, there is little opportunity for heat recycle in the column.

All TMRs within the range selected are below unity, which should encourage movement of heat upwards. Reducing TMR should also encourage a small movement upwards in the location of heat input. This is seen to some degree with a small shift upwards in bulge maximum and CO_2 absorption as the TMR is reduced. As with the other systems, at high TMRs and low loadings, the heat of reaction escapes with the rich amine. Reducing TMR gradually decreases the driving force at the bottom of the column, which allows heat generation to move up the column and elevates the bulge. At the same time, lower liquid thermal mass decreases heat recycle from the exiting vapor to the incoming lean solvent, which causes the magnitude of the bulge to decline. Since the system is never near a rich-pinch, and the location of heat input does not significantly shift towards the middle of the column, the maximum bulge temperature is never extreme. There is little heat recycle, and the difference in bulge temperature between the selected TMRs is relatively low.

As seen in the three systems studies, for systems where rich-end pinch occurs near or above a TMR of one, the bulge temperature moves rapidly with small changes in the TMR. The bulge moves rapidly upwards primarily due to an approaching rich-end pinch. It declines rapidly primarily through acid gas breakthrough when a pinch does occur.

For high concentration solvents, the bulge temperature moves in accordance with the effects of movement of the location of the heat input. However, if rich pinch is far away, this location shift is minimal, and the net result is a bulge temperature that does not move significantly.

Systems whose solvent concentration require traversing a TMR of unity *near a rich-end pinch* produce the highest temperature bulges of all solvent concentrations. This system has high ability to recycle heat due to a TMR near unity, and sufficient opportunity exists for recycle as the location of heat input has been elevated. The concentration that produces this scenario for a given solvent varies with the acid gas concentration in the sour gas.

Real World Application

Canyon Midstream's James Lake Plant (JLP) provides an example of how elevated temperature bulges can exist in systems even if not shown by instrumentation. Once a plant is built, changing the TMR significantly may not be a possibility. However, these high bulges could be resolved by the elimination of a rich-end pinch without requiring significant changes to the system's TMR.

The James Lake Plant is a 110 MMSCFD gas plant just outside of Odessa, TX, processing gas gathered from approximately 90 miles of trunk line in the Central Basin. Operations began at the facility in 2014.

In the summer of 2017, a DGA acid gas removal system began to exhibit signs of accelerated degradation rates. Upon discovery of these signs, Canyon Midstream investigated potential causes of the degradation. An initial simulation of the system is shown in Figure 17.



Figure 17: Initial Simulation of JLP Amine Absorber showing Normal Operation

According to operations, the amine system was treating adequately, and there appeared to be nothing out of the ordinary, which the simulator seemed to confirm. However, a further investigation by the plant engineer, including a thermal scan of the absorber, revealed an unexpectedly high temperature bulge in the system. This scan can be seen in Figure 18 below:



Figure 18: Thermal Scan of Amine Absorber Showing Extremely High Temperatures on Middle Trays

The scan showed the column temperatures exceeded 215 °F with the bulge shifted toward the middle of the column. However, the simulations performed during the initial study did not indicate

any trouble or high temperature bulge. A graph comparing the simulated temperature profile to the profile obtained from the scan can be seen in Figure 19:



Figure 19: Thermal Scan Results as Compared to Original Simulation Temperature Profile assuming 50 wt% DGA

An amine analysis discovered that the solvent strength was 32.8 wt% DGA, not the assumed strength of 50 wt%. The simulation was adjusted to reflect the actual solvent strength, not the assumed strength. The results of the second simulation, and as seen in Figure 20, showed a temperature profile similar to the original thermal scan.



Figure 20: Thermal Scan Results as Compared to Simulation with 33% DGA

Although the driving force was relatively tight across the column as it experienced the high temperature bulge, as shown in Figure 21, the system was still able to treat to acceptable levels.



Figure 21: Driving Force Profile of JLP Amine Absorber with 33% DGA

A comparison of the 32.8 wt% and 50 wt% simulations showed that an increase in solvent strength should resolve the high bulge temperature. The solvent strength was increased to 50 wt%, and a second thermal scan was performed on the system, shown in Figure 22.



Figure 22: Second Thermal Scan of JLP Amine Absorber with 50% DGA

This second thermal scan agreed with the temperature profile of the original, 50 wt% DGA simulation, as shown in Figure 23. Moving the bulge down the column allowed the heat to leave with the rich amine. Note the significant increase in liquids temperature on tray 20 (135 °F) as compared to the 32.8 wt% DGA case (100 °F). The reverse is true for the vapor where the 50 wt% case showed a much cooler temperature (135 °F) as compared to the 32.8 wt% case (150 °F). As is the case, monitoring only exit flow temperatures is misleading as to the conditions inside the tower.



Figure 23: Second Thermal Scan Results as Compared to Original Simulation using 50% DGA

With the reduced temperatures and increased solvent strength, driving force along the bottom of the column also increased significantly, as seen in Figure 24.



Figure 24: Driving Force Profile of JLP Amine Absorber using 50% DGA

For the JLP system, there were actually two possible solutions to reduce the maximum temperature bulge. One was to move the bulge downwards by increasing TMR (reducing TMR was not possible as it would have allowed acid gas breakthrough). Increasing the solvent strength was also an option, which would move the system to a completely new "operating curve". Figure 25 shows the 32.8 wt% DGA concentration curve and the 50 wt% DGA concentration curve for the JLP feed composition.



Figure 25: Maximum Temperature Bulge Curves for the before-and-after Solvent Strengths for JLP Amine System

As can be seen from the figure, a TMR increase from 0.74 to 0.87 on the 32.8 wt% curve would have only reduced the temperature bulge to 200 °F, a value still unacceptably high. Meanwhile that change equates to a 20% increase in amine circulation rate. A circulation increase of 30% would be required to reduce the bulge to 180 °F. This increase in circulation, providing no other benefit than to reduce the bulge temperature, was operationally unacceptable.

Meanwhile, an increase in the solvent strength moved operations to an entirely new temperature vs. TMR curve. This resulted in a bulge temperature *significantly* lower, 165F, while slightly *reducing* the TMR.

Similar behavior can be seen in Figure 9 for systems with practical TMRs to the left of unity. In all of these systems, the magnitude of the temperature bulge can be reduced by increasing the solvent strength. For example, a solvent strength of 40 wt% and a TMR of 0.8 yields a maximum bulge temperature of 190 °F in Figure 9. Simply increasing the solvent strength to 50 wt% reduces this bulge temperature to 177 °F. This is achieved without any change to the TMR.

Conclusion

If an amine absorber is considered an analog of a heat exchanger, then it is true that the greatest heat transfer between the phases can occur when TMR is equal to one. However, the location and magnitude of heats of reaction in the system has a significant impact on the location and size of the temperature bulge. The location and magnitude of the temperature bulge are also a function of the acid gas concentration and the solvent strength. For a specific system, these factors may result in a maximum absorber bulge at TMRs greater than or less than one.

As seen in the James Lake Plant, due to limitations in instrumentation, high temperature bulges can exist in systems without the operator knowing it. Understanding how these bulges behave, and being able to predict their existence based on what instrumentation exists, is therefore important. While increasing circulation (i.e. increasing TMR) is an option to reduce the

magnitude of temperature bulges, adjusting the solvent strength to avoid rich-pinch conditions can be a more effective means of doing so. In fact, in almost all cases, increasing solvent strength should reduce the magnitude of the temperature bulge without any adjustment to the solvent circulation rate.

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