

Glycol Dehydration as a Mass Transfer Rate Process

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ABSTRACT

Glycol dehydration is a process that presents some unique challenges from technical and computational standpoints. In the first place, modern designs almost invariably use tower internals consisting of structured packing rather than the more traditional bubble cap trays. Structured packing offers lower pressure drop and considerably higher capacity than trays, and it is well suited to handling the very low L/G ratios common in dehydration. However, until now estimating height of packing used rules of thumb, not science. Mass transfer rate-based modeling, on the other hand, uses science and therefore offers greater reliability of design. The other challenge of dehydration using any glycol is thermodynamic.

The dehydration of streams having very high concentrations of acid gases is hard to model reliably because the thermodynamics of vapor-liquid phase equilibrium involves water, one of nature's most perversely-nonideal chemical species. Interactions between water and the acid gases CO₂ and H₂S, as well as with most hydrocarbons in the gas phase must be taken into account for a thermodynamic model to be reliable. Furthermore, in the liquid phase, aqueous glycol solutions themselves are quite nonideal because both water and glycol are polar molecules.

There are other facets of glycol dehydration that are interesting just from an applied science viewpoint. One of them is the heat transfer situation that ensues in a regenerator using both stripping gas and a reboiler (Stahl column). When the hot gas hits the bottom of the packing in the wash section atop the column it finds itself going from an environment in which it is saturated with the water contained in a predominantly TEG stream into an environment where it is grossly *under*-saturated with respect to the pure water stream in the wash section. This humidification process extracts the necessary heat of vaporization as sensible heat from the liquid water phase and this can drop the wash water temperature by 30°F, 40°F or even more.

Optimized Gas Treating, Inc. has recently released a new glycol dehydration model, currently for TEG, and being extended to MEG and DEG. This paper addresses the efficacy of the model in terms of (1) how well it reflects known phase behavior and (2) how closely it **predicts** known plant performance data using both bubble cap trays and packed columns *without recourse to HETP or HTU estimates and other rules of thumb.*

Phase Equilibrium

The concern here is with the accurate calculation of equilibrium water content of high- and low-pressure gases containing very high levels of CO₂ and/or H₂S. The ProTreat™ simulation tool's dehydration model uses the Peng-Robinson equation of state (EOS) for the vapor phase and currently offers a 4-suffix Margules equation activity coefficient model based on the data of Bestani & Shing (1989) for the liquid phase as reported by Clinton et al. (2008). A similar model based on the less conservative data of Parrish et al. (1986) is planned for a future release.

There are two important aspects to thermodynamic modeling: water content of the treated gas and the solubility of hydrocarbon, acid gas, and especially the BTEX in the water-laden glycol. Table 1 compares ProTreat model results with GPSA Data Book entries for saturated water content. Generally, ProTreat reproduces measured values of water content to within the accuracy of the data. The Peng-Robinson EOS that performs these saturated water content calculations applies a large number of interaction parameters (k_{ij} 's) for the interactions between water and the various gases as well as between the gases themselves as outlined, for example, by Carroll and Mather (1995).

Table 1 Saturated Water Content of Gases

GPSA Ref.	Mole Percent (Dry Basis)			Temp (oF)	Pres (psia)	H ₂ O lb/MMscf	
	CH ₄	CO ₂	H ₂ S			Meas'd	ProTreat
Ex 20-1	100	0	0	150	1,000	220	216
Ex 20-2	80	20	0	160	2,000	172	188
Fig 20-9	0	100	0	100	500	132	125.3
					750	110	102.5
					1,000	125	100.7
					2,000	215	215.1
					3,000	238	247.8
	5.31	94.69	0	100	850	88	96.9
					1,125	81	99.2
					1,500	128	148.6
					2,000	139	184.2
					2,000	40.6	41.1
					1,000	286	283.9
					2,000	40.6	45.1
Fig 20-16	89	11	0	100	2,000	282	292.5
	89	11	0	160	1,000	172	188.5
	80	20	0	100	2,000	111	103.5
	80	20	0	160	1,000	247	252.6
	80	20	0	160	2,000	292	293.4
	92	0	8	130	1,500	81	81.2
	72.5	0	27.5	160	1,367	442	264.4
	83	0	17	160	1,000	109.2	95
	30	60	10	100	1,100	164.6	234.5
	9	10	81	100	1,900		
	5.31	94.69	0	77	1,500		
	5.31	94.69	0	122	2,000		

Other components whose solubility in TEG is pertinent are the acid gases and hydrocarbons, especially the BTEX components. Vapor-liquid equilibrium constants (K-values) for benzene, toluene, ethyl benzene and o-xylene are available in GPA RR-131 and the data there have been used to fit the ProTreat solubility model for these species. The data indicate that at typical contactor conditions approximately 10–30% of the aromatics in the gas stream may be absorbed in the TEG solution. ProTreat results conform closely to the conclusions of RR-131 (as they should, because ProTreat's solubility model has been regressed to the actual measured BTEX solubilities).

Process Simulation

The GPSA Data Book contains a nice example of dehydration with TEG (Example 20-11). The gas is water saturated at 600 psia with other details noted in Figure 1. Two cases are detailed, both requiring two theoretical stages. One uses bubble cap trays which at a tray efficiency of 25 to 30%, translates into 6 to 8 actual trays. The other case uses 10-ft of an

unspecified structured packing. ProTreat has provision for a separate Stahl column, shown immediately below the stripper in Figure 1 but the stripper can also be simulated without this column if desired. Two condenser outlet streams allow wet stripping gas withdrawal from the system (Stream 19), and removal of a specifiabile portion of condensed water (Stream 20), with the remainder returned as reflux.

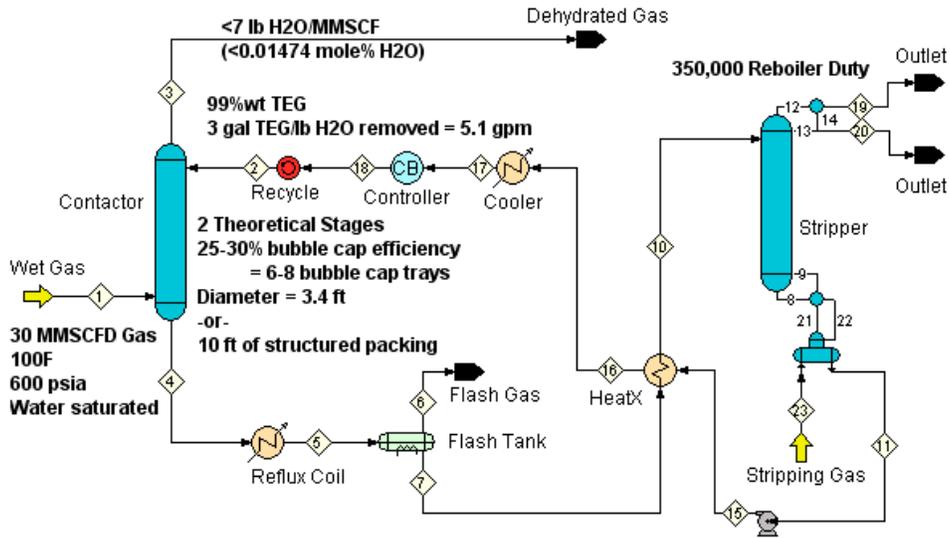


Figure 1 GPSA Data Book Example 20-11

Table 2 shows the effect of the actual tray count on the water content of the dehydrated gas. ProTreat simulation indicates 6 trays are adequate to reduce the water content from 88.7 lb/MMscf to the target level of < 7 lb/MMscf (32°F Dew Point). Tower diameter for 70% flood is 3'-0". These values are in line with GPSA data book results which are annotated in Figure 1. In summary, the available data indicate that the model is accurately reflecting literature data on the VLE and general experience as reported by GPSA.

Table 2 Water Content vs. Tray Count

Number of Trays	Water lb/MMscf
5	8.5
6	6.7
7	5.7
8	5.1

Dehydration Column Performance

Until now only an equilibrium stage model has been available for calculations involving the performance of structured packing. However, packing size is surely related to the HETP of the particular packing. Packing size can be expressed in terms of specific surface area and crimp

size, characteristics that are geometrically related. Under otherwise identical process conditions, one should expect that large crimp packing will require a much deeper bed to give the same performance as a relatively short bed of small crimp packing simply because the surface area of the small crimp material is considerably higher.

Figures 2 and 3 simulate how packing size within the Mellapak X-series (higher crimp angle) packings affects dehydration performance. For Sulzer Mellapak structured packings, the packing designation, e.g., M250.X is an approximate indicator of the specific area, in this case $250 \text{ m}^2/\text{m}^3$. Simulations were all run with 40-ft of packing and the absorber was sized for 70% flood (9 to 11 ft diameter depending on crimp size). The absorber was set up to dehydrate 49,000 lbmol/hr of wet sweet methane (trace CO_2 and H_2S) using 250 gpm of 99.95 wt% TEG at a nominal tower pressure of 200 psig. The gas-phase temperature profiles for the various packing sizes shown in Figure 2 indicate that there is a significant temperature bulge in dehydration columns, caused by the change of phase of the water being absorbed. Water absorption generates sensible heating equivalent to its latent heat of condensation. Also, when small-crimp packings are used, the temperature bulge is closer to the bottom of the column because water absorption is much more rapid with the larger surface area. Figure 3 shows the water content of the gas at various positions along the height of the column. It is evident that after traversing the bottom 20 feet of M350.X packing the gas is about as dry as 99.95 wt% TEG at 100°F can get it. With M125.X packing on the other hand, water is still being removed even after the gas has passed through 40 feet of packing. **So the bed height needed is very much a function of the packing size.** It is not that rules of thumb (ROT) cannot be made to work; rather, it's that the right ROTs, at least for packing, depend on too many parameters (not just packing type and size but also on the gas and solvent fluxes through the column) and this makes them not reliably available. Until now the answer to this dilemma has been to over build the columns; however, in a competitive environment, surely being able to avoid over design puts the knowledgeable contractor and the astute internals vendor in a commercially advantageous position. Mass transfer rate based simulation is the precise tool that allows this to be done.

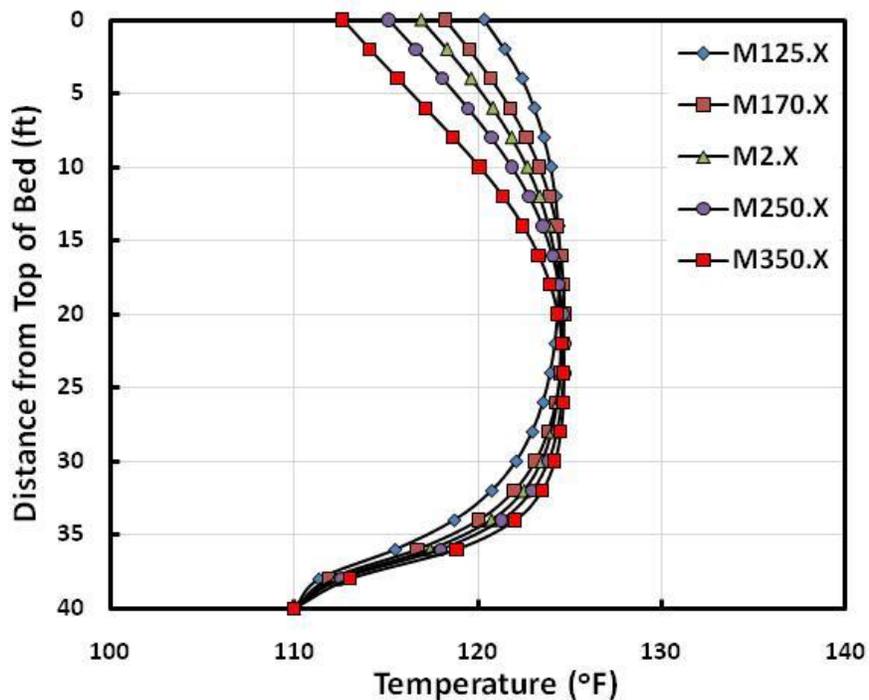


Figure 2 Temperature Profiles and the Effect of Packing Size in the Mellapak M Series

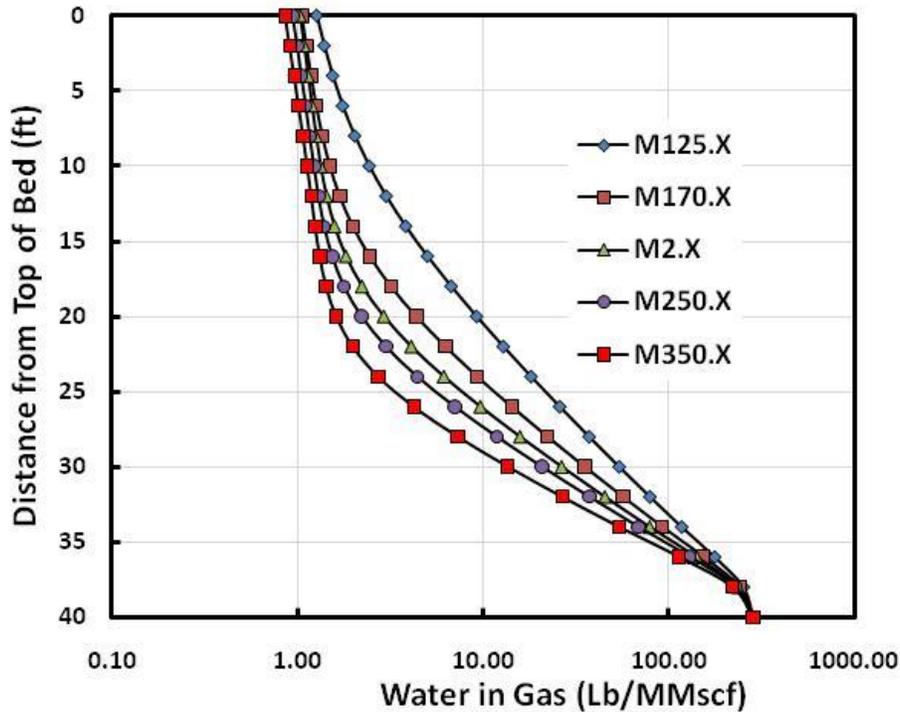


Figure 3 How Water removal Depends on Packing Size and Packed Bed Depth

Figure 4 shows that the ROT of 6 to 8 trays for dehydration is a gross over simplification. The number of trays depends at least on the dryness to be achieved, i.e., the dryness of the solvent. If the target dew point is not too stringent (e.g., 10 or 20 lb H₂O / MMscf) then 6 or 8 trays seem adequate. But in very low dew point applications such as LNG plants two or three times that number of trays may be required to get to the desired dryness. With 99.97% TEG, for example, it is possible to get to below 1 lb/MMscf water content, but even after 16 trays, water is still being removed.

For the particular conditions simulated in this study, it should be mentioned that high TEG viscosity is a consideration and will negatively affect internals performance compared with light hydrocarbons for example. At the solvent moisture levels encountered in these simulations, viscosity is not significantly affected by water content, and at the lowest temperature (feed solvent at 100°F) the viscosity is about 19 cP (for reference, corn syrup is 50–100 cP). This does not necessarily eliminate the possibility of using trays, although it does tend to make structured packing more attractive.

Stahl Columns and Stripping Gas

A Stahl column gives an extra stage of regeneration by taking the solvent from the reboiler and contacting it with a flow of dry stripping gas. Stahl columns are essential when the very treated gas must be of very low dew-point. Figure 5 shows the effect of stripping gas rate (SCF per gallon of TEG solvent) on the TEG purity and on the water content of the treated gas for Example 20-11 from GPSA Data Book scaled up by a factor of five and using 6 bubble cap trays in the absorber and a 10-ft bed of FLEXIPAC 1.6Y in the regenerator (includes a 2-ft reflux wash section). In terms of scale, the absorber is nearly 7-ft diameter and is drying gas that is water-saturated at 600 psia and 100°F. The regenerator is only 15-in diameter.

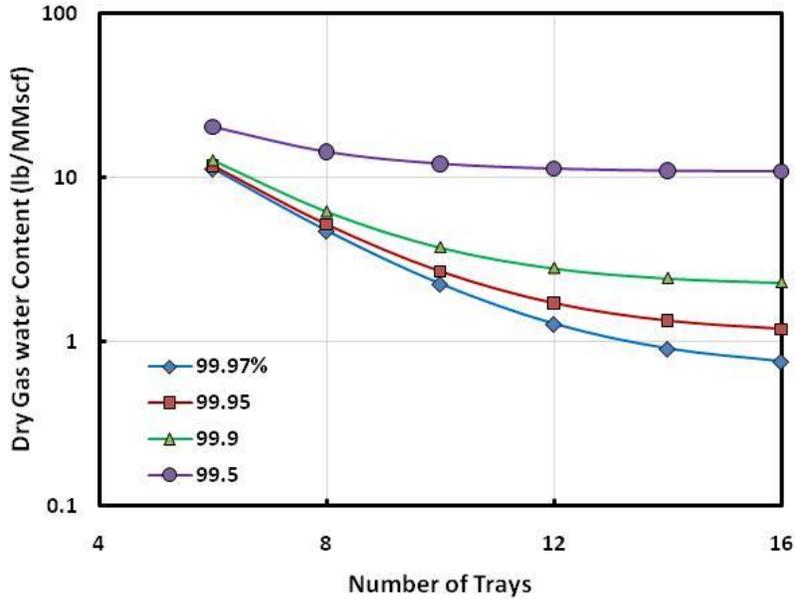


Figure 4 Water Removal to Low Dew Points Requires Deeper Beds and More Trays

The simulation results in Figure 5 show that using even a modest flow of stripping gas can reduce the water content in the treated gas by more than a factor of two. It removes more water from the solvent and increases the dry TEG from 98.8 wt% to 99.8 wt%. This particular treated gas is dry enough by transmission line standards, but it's a long way from dry enough for an LNG plant, for example. However, this demonstrates the principle that a Stahl column can serve a useful purpose—it would be used when treated gas needs to be drier than usual.

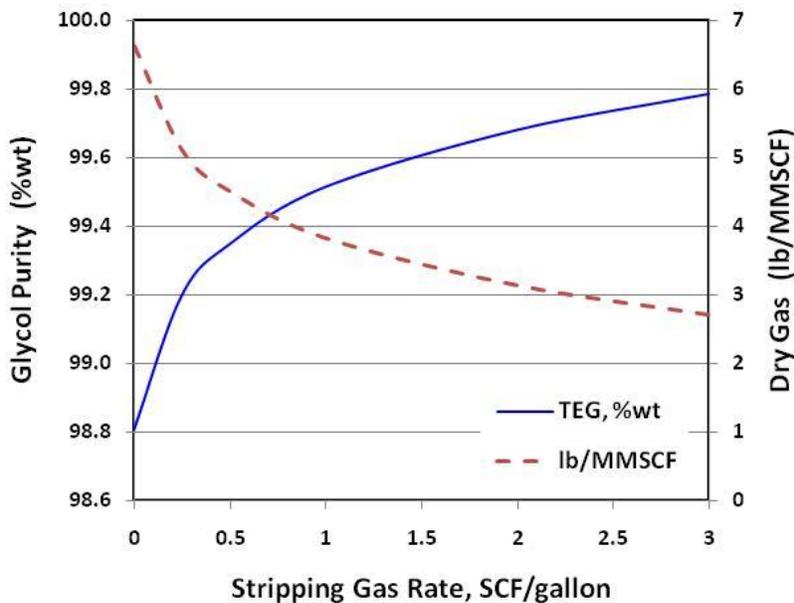


Figure 5 Effect of Stripping Gas Flow on Solvent Dryness and Gas Water Content

Interesting Observations from a Mass Transfer Rate Model

The mass transfer rate model uses real trays both in number and mechanical detail, and real packing in terms of actual bed depths of a specific packing with defined geometry including crimp angle, crimp size, surface treatment, and specific surface area. The simulation of a packed column begins with finely segmenting the packed height to approximate the continuous nature of contacting by using a large number of thin cross-sectional slices. As a result, the mass and heat transfer effects can be observed on a fairly detailed scale.

Figure 6 shows the vapor and liquid temperature profiles through a 10-ft deep bed of 2-in metal Nutter Rings. The bed starts with a 2-ft deep wash section for TEG recovery followed by an 8-ft deep stripping section for water removal. The stripper was simulated by dividing it into 40 segments, each having a 3-in depth. Finer segmentation is, of course, possible but it adds nothing to the detail and very little to the accuracy of the simulation. We will traverse the regeneration column starting with the condensate (essentially pure water) which enters the column at 180°F and is heated by the gas stream (stripping gas and water) which is at 198°F.

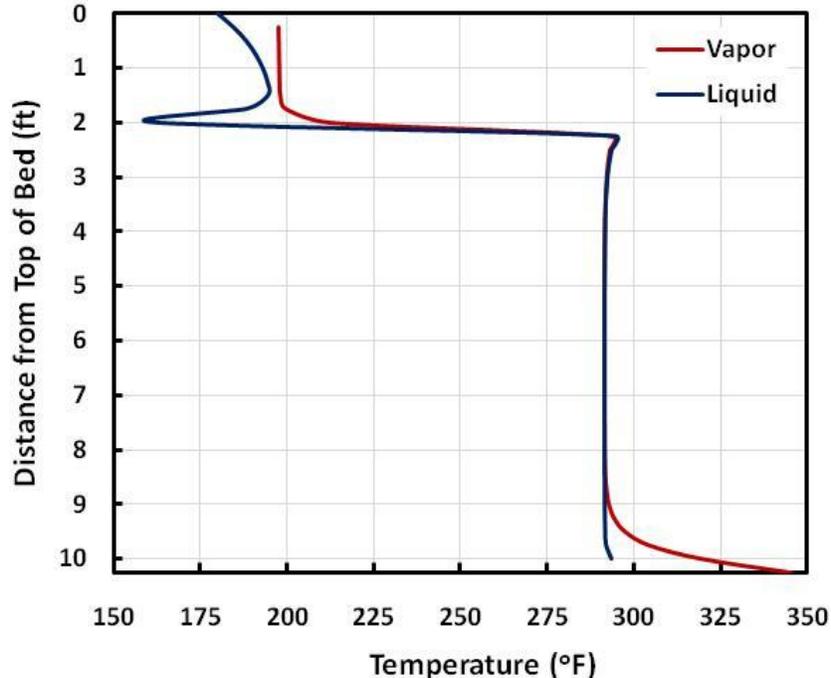


Figure 6 Effect of Stripping Gas Flow on Solvent Dryness and Gas Water Content

As the condensate trickles through the bed it continues to be heated by the wet stripping gas, but within the first 18 inches its temperature reaches a peak (194.5°F) and then suddenly plummets to about 160°F. The gas becomes hotter as one descends through the column and eventually experiences a rapid climb to 294°F. The question is why these trends should not be a surprise. The answer for the gas phase is relatively simple: feed, preheated to 300°F enters the column at the 2-ft level and flashes into its vapor and liquid parts. The fact that the vapor temperature changes radically at the feed point is simply the result of the hot feed meeting a cold reflux water stream. *But why does the reflux water cool so much?*

When the vapor leaves the top of the stripping section its water content is very nearly in equilibrium with the liquid in the stripping section. The liquid there is better than 95 wt% TEG and only 5 wt% (17–18 mol%) water. This vapor is suddenly exposed to a pure, hot water stream coming from the wash section so it is seriously under saturated against pure water. The reaction then is for water to evaporate as fast as possible to re-saturate the hot gas. This is a typical humidification operation and has some interesting characteristics. The evaporation process is not *mass transfer rate* limited! Rather, it is limited by the rate at which the latent heat of vaporization demanded by the humidification process can be drawn from the bulk liquid to the gas-liquid interface. This process is one of heat transfer and, indeed, the rate of humidification right above the feed point is controlled by essentially conductive heat transfer across the liquid film running over the packing. *The process is heat transfer rate limited.* The mass transfer driving force for humidification is so high that enough heat is drawn from the reflux water to cool it, in this case by approximately 33°F.

As the bottom of the stripping section is approached, liquid meets increasingly hotter vapor coming from the reboiler (bubble point is quite sensitive to water content when the water is low). This cools the vapor and heats the liquid, and again some of the heat transfer is a result of water transferring from the vapor back into the liquid around the bottom part of the stripping section.

Figures 7(a) and (b) are intended to show how the use of stripping gas affects these temperature profiles. The plots are for an 8-ft bed of FLEXIPAC® 1.6Y structured packing with 2-ft top wash section for TEG recovery. Even when stripping gas is not used, the condensed water leaving the reflux section meets a much hotter gas and a good part of the temperature equilibration takes place by water evaporation from the reflux stream. This is again a humidification process and the reflux water cools as a result of the demand for latent heat for vaporization. In Figure 7(b) the presence of stripping vapor dilutes the gas leaving the stripping section, and this results in slightly more driving force for humidification from the additional water holding capacity of the stripping gas. (How much the stripping gas adds to driving force and capacity depends on the relative flows of stripping gas versus reboiler vapor.) Again, the reflux water temperature peaks and then drops from 197°F to about 141°F, for a total cooling of 56°F, the same as for the no-stripping gas case. However, with stripping gas (N₂) the temperature bulge in the reflux section is a consequence of the dilution by nitrogen. We note in passing that to maintain water balance the no-stripping-gas case required a 212°F condenser temperature versus 180°F for the case with stripping gas.

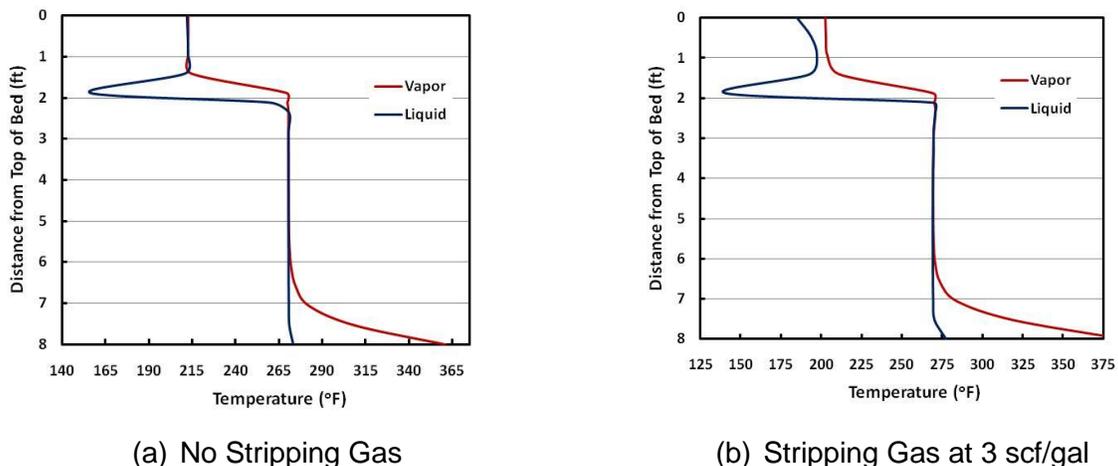


Figure 7 Effect of Stripping Gas Flow on Temperature Profiles

Factors That Affect Dehydration of Sweet Gases

To learn more about the practical limits of glycol dehydration, a sensitivity analysis was conducted starting with the 3 SCF/gallon stripping gas rate at 1.72 MMBtu/hr reboiler duty referenced in the preceding section. First, reboiler duty was increased to 2.5 MMBtu/hr which amounted to an increase from 1124 Btu/gallon to 1634 Btu/gallon. This change allowed the glycol purity to increase from 99.79 wt% to 99.96 wt% TEG. The water content of the dehydrated gas was predicted to drop from 2.7 lb/MMscf to 2.0 lb/MMscf assuming 6 bubble cap trays for contacting. This is not much of an improvement for nearly a 50% increase in reboiler energy. Are there enough absorber trays to take advantage of the greatly improved TEG dryness?

The number of glycol contacting trays was next increased from 6 to 8 while maintaining the lean glycol purity of 99.96%wt. This dropped the water content of the gas by an order-of-magnitude, from 2.0 lb/MMSCF to 0.2 lb/MMSCF, so much for ROT.

Finally, at 12 trays of dehydrator contacting, some of the reboiler duty was traded for stripping gas. Lowering the reboiler duty from 2.5 to 2.0 MMBtu/hr and doubling the stripping gas rate (from 3 to 6 SCF/gallon) resulted in a predicted water content of 0.13 lb/MMSCF. At this water content, the gas dew point can be expected to be well below the hydrate formation temperature. Simulated glycol purity was 99.975%wt. So it appears that stripping gas is a more effective way to improve dehydration system performance compared to brute force reboiler duty increase.

There is much that can be learned by playing with a mass transfer rate model, even for a well-proven process such as glycol dehydration. The rate model allows one to probe the limits of what is in practice possible, for example trading expensive reboiler duty for possibly cheaper stripping gas, or optimizing dehydration unit performance in a demanding LNG setting. Because this kind of tool is so reflective of the real physics, the real chemistry, and the real engineering going on in an amine, DMPEG or glycol plant, using the tool as a virtual laboratory and pilot plant is very attractive.

Dehydration of Acid Gases

Down-well disposal of acid gases (so-called acid gas injection) requires the gas to be compressed to very high pressure. If the gas is wet, compressing it will cause liquid water to drop out and this liquid will be saturated with acid gas at high pressure. Unless one is prepared to build compressors and other equipment from unobtainium, it is paramount that the water be removed from the gas *before* compression. Therefore, it is of interest to compare dehydration of otherwise pure but water saturated H₂S with dehydrating the equivalent sweet gas volume.

In order to keep liquid water away from the compression train at pressures up to about 1000 psig, Figures 20-7 through 20-9 in the GPSA Data Books imply that dehydration to below about 100 lb H₂O/MMscf may be required for some compression paths. A glycol contactor pressure of 10 psig was chosen assuming that acid gas came from a typical amine regenerator operating at 12-15 psig. Assuming an 80:20 mixture of H₂S and CO₂ saturated with water was to be dehydrated; ProTreat predicted that 5 gallons of 99.4%wt TEG would be required for each lb of water removed. Assuming the same glycol was circulated to scrub water-saturated sweet gas at 10 psig, water content in the dehydrated gas was predicted to be 10% lower than in the dehydrated acid gas, or nominally 91 lb/MMScf. So besides being stinkier in general, acid gas is tougher to dehydrate than same amount of sweet gas. Fortunately however for acid gas, this is traded off by a minimum in the water solubility at moderate pressures which may preclude the need for dehydration in some cases.

Conclusions

Rules of thumb are fraught with danger because often the rules simply do not apply. A blanket tray efficiency of 25% is close to the truth most of the time. But in deep water removal via glycol dehydration, 25% is optimistic and unless one adds several additional “safety” trays, failure may be imminent. The situation with packing, be it random or structured, is much worse. Quoting or recommending a single HETP or HTU value can be very dangerous. The right value depends on the packing type as well as on the operating conditions and the gas dryness sought. ROTs had their place when equilibrium stage calculations were the best available tools and reliance had to be placed on experience as expressed (and mis-expressed) in ROTs. Today we have available powerful mass transfer rate based simulation tools and reliance on rules of thumb and other approximations and guesstimates is no longer warranted.

The beauty of ProTreat’s mass transfer rate based approach to simulation is that one never has to worry about tray efficiencies, artificial residence times, HETPs, HTUs, and other rules of thumb. ProTreat doesn’t use rules of thumb—it uses science and good sound engineering to **predict** performance. These results were all obtained without any correction factors whatsoever. They are true predictions in every sense of the word.

Literature Cited

Bestani, B., Shing, K. S., *Infinite dilution activity coefficients of water in TEG, PEG, glycerol and their mixtures in the temperature range 50 to 140°C*, Fluid Phase Equilibria, vol 50, 1989

Clinton, P., Hubbard, R. A., Shah, H., *A review of TEG-water equilibrium data and its effect on the design of glycol dehydration units*, Laurence Reid Gas Conditioning Conference, Norman, OK, 2008

Parrish, WR, Won, KW, Baltatu, ME, *Phase Behavior of the Triethylene Glycol-Water System and Dehydration/Regeneration design for Extremely Low Dew Point Requirements*, Proceedings of the 65th annual convention of the GPA, San Antonio, 1986

Research Report RR-131 *The Solubility of Selected Aromatic Hydrocarbons in Triethylene Glycol* - H.-J. Ng, C.-J. Chen, D. B. Robinson, DB Robinson Research Ltd., Edmonton, Alberta. Project 895. December 1991

Carroll, J.J., Mather, A.E., *A generalized correlation for the Peng-Robinson interaction coefficients for paraffin-hydrogen sulfide binary systems*, Fluid Phase Equilibria, vol 105, 1995
Engineering Data Book, Gas Processors Supplier’s Association, 12th Edition, Vol II, Ch. 20.