Influence of Process Operations on VOC and BTEX Emissions from Glycol Dehydration Units

MICHAEL W. HLAVINKA, VICENTE N. HERNANDEZ-VALENCIA, JERRY A. BULLIN,
Bryan Research & Engineering, Inc.,
Bryan, Texas

ABSTRACT

Over the past several years, concerns about hydrocarbon emissions from the regenerator vent in glycol dehydrators has become a significant issue. This paper illustrates the prediction capabilities of PROSIM® for analyzing these concerns. First, the paper illustrates that predictions made by PROSIM compare favorably to data from the API Glycol Reboiler Emissions Work Group. Next, PROSIM shows that while a significant amount of non-aromatic VOC emissions are released in the flash separator, a small fraction of BTEX emissions are evolved at normal conditions. PROSIM indicates that over-circulation does not enhance dew point depression, but will cause a nearly linear increase in the amount of BTEX compounds emitted from the unit. Next, various contactor pressures are analyzed which show that higher emissions result from lower pressure units due to the increased amount of water that must be absorbed. Finally, a comparison between DEG and TEG facilities with similar circulation rates indicates that approximately 30-40% more BTEX emissions occur when using TEG than DEG.

Proceedings of the Seventy-Second GPA Annual Convention. Tulsa, OK: Gas Processors Association, 1993: 100-106.
"Calculation of VOC and BTEX Emissions from Glycol Dehydration Facilities". Presented at the 1992 Gas Research Institute, New Orleans, LA, 1992

INTRODUCTION

A common method to remove water from natural gas is glycol dehydration.[1] In this process, triethylene glycol (TEG) or diethylene glycol (DEG) is used to remove the presence of water in the gas stream. Water vapor can cause hydrate formation at low temperatures and high pressures or corrosion when it is in contact with hydrogen sulfide (H_2S) or carbon dioxide (CO_2), components regularly present in the gas stream.

Glycol dehydration units are typically represented by a contactor, a flash tank, heat exchangers, and a regenerator, as shown in Figure 1. The glycol, usually TEG, enters at the top of the contactor and absorbs water as it progresses toward the bottom of the column. A dry gas exits at the top of the contactor and may be used for cooling the incoming lean glycol.

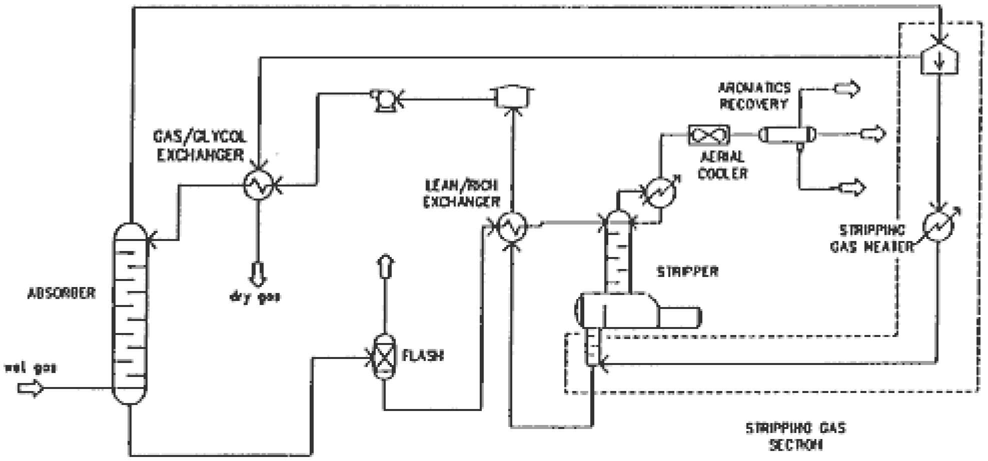


Figure 1. Typical glycol dehydration unit.

The rich stream flows to a separator or Flash tank where gaseous hydrocarbons that were absorbed along with some of the water in the contactor are liberated and used as fuel. Finally, the glycol flows to the stripper where it is regenerated by boiling off the water and returned to the contactor. For processes requiring gas with very low water dew points, a stripping vapor will most likely be needed to aid the regeneration process. This technique is illustrated by the region enclosed in the dotted line in Figure 1. For maximum stripping, this vapor is normally injected into a short column at the bottom of the reboiler. However, the gas may also be introduced directly into the reboiler.

In the past years, glycol dehydration plants have been designed using rule-of-thumb procedures. While still sufficient for many applications, today more efficient designs are often required. In many cases, the plant feed will contain small quantities of aromatic hydrocarbons that are quite soluble in TEG. The aromatics are primarily comprised of benzene, toluene, ethylbenzene, or xylenes (BTEX). These aromatics are carried to the flash tank where a small fraction are released along with other volatile organic compounds (VOC’s). The remaining VOC’s and aromatics travel to the regenerator where the application of heat will remove virtually all volatile gases. Since the regenerator is usually vented to the atmosphere, the plant may have serious environmental impact, even in small plants where the total aromatic emissions can easily exceed 100 Ib/day.[2]

This paper presents the progress of current work to modernize simulation software used in design and optimization of dehydration units. In this effort, attention has been placed on providing a tool that can be used to address environmental concerns as well as other process concerns. In the first section of the results, the calculations are compared to actual plant data presented by the API Glycol Reboiler Emissions Work Group.[3] After validation, the emissions from the regenerator and flash tank are presented for a typical facility at various circulation rates and flash tank conditions. Next, the effect of contactor pressure on BTEX emissions is investigated. Finally, a comparison in emissions between a TEG and DEG unit is given.

DESIGN OF DEHYDRATION UNITS

When optimizing the design of dehydration facilities for maximum dew point depression, the impact of the following parameters should normally be considered:

1. Number of trays in the contactor
2. Glycol circulation rate through the contactor
3. Temperature of the reboiler in the regenerator
4. Amount of stripping gas used, if any
5. Operating pressure of the regenerator

Of the above parameters, only the first four are normally considered as variable parameters. The first two parameters affect the approach to equilibrium at the top of the absorber while the third and fourth dictate the value of the equilibrium water content by limiting the purity of the lean glycol to the absorber. The fifth parameter affects the lean glycol purity in a manner similar to reboiler temperature. However, the vast majority of units are vented to the atmosphere so this parameter is beyond control.

In addition to the design parameters listed above, several other factors influence the residual water content of the sales gas. However, often these factors are fixed and cannot normally be changed when optimizing a unit. First, the temperature of the inlet gas will dictate the total amount of water fed to the unit. Lower plant inlet gas temperatures will require less water to be removed by the glycol. Second, lean glycol temperature at the top of the contactor will affect the water partial pressure at the top stage. Consequently, high glycol temperatures will result in high water content in the overhead gas. However, this temperature is normally no cooler than 10°F above the inlet gas to prevent hydrocarbons in the feed from condensing in the solution. This limit is normally maintained by a gas/glycol exchanger that cools the lean glycol to approximately a 10°F approach using the dry gas.

Other parameters in the plant have limited or no effect on the dry gas water content. The number of equilibrium stages in the regenerator has only a slight effect on the lean glycol purity. Equilibrium at the reboiler temperature and pressure is approached in the reboiler so that additional stages have no effect. The operating temperature of the lean/rich glycol exchanger only impacts the reboiler heat duty and has little influence on dehydration ability.

The significant parameters that affect the amount of hydrocarbons emitted in the regenerator vent of existing dehydration facilities include:

1. Amount of BTEX hydrocarbons in the plant feed
2. Glycol circulation rate through the contactor
3. Contactor pressure and temperature
4. Separator operating conditions

Of these parameters, only the second and fourth can be varied. As stated above, the circulation rate affects the approach to equilibrium obtained at the top of the absorber. Normally a minimum of 3 gal TEG/lb water removed is required to approach equilibrium sufficiently so that proper dehydration occurs. The separator normally removes a significant quantity of non-aromatic VOC’s. However, as shown later in this paper, aromatics are only removed in the flash at high temperatures and low pressures.

PROCESS CALCULATIONS AND COMPARISON TO DATA

The capabilities of Bryan Research & Engineering’s glycol dehydration program, DEHY®, have been integrated into the general purpose process simulation program, PROSIM, and expanded to better predict hydrocarbon and aromatic solubility in glycol. All calculations provided in this report are based upon calculations made with PROSIM. PROSIM allows the user to draw the process flow diagram on the computer screen and enter the operating parameters on "pop-up" forms. The program is sufficiently flexible to handle almost any glycol dehydration scheme. Additionally, PROSIM has heavy ends/crude characterization, complex heat exchanger, tray rating, and a variety of utility calculational operations. Dehydration results obtained by PROSIM have been compared to plant data, obtained by Worley in the GPSA Engineering Data Book[4] and other pertinent experimental vapor-liquid equilibrium data as noted throughout this report.

To determine the validity of PROSM in modeling BTEX emissions from dehydrators, the results were compared to data provided by the API Glycol Reboiler Emissions Work Group.[3] This work included BTEX emission data from ten operating facilities located in Louisiana, Oklahoma, and Texas. One of these plants (labeled "West Texas Glycol Unit" in the API work) used stripping gas in the reboiler and a separator supplemented with purge gas. Since no information on this gas was available, the facility was not modeled for this paper. This unit also included a static mixer instead of a trayed absorber.

A comparison of the measured BTEX emissions to those estimated by PROSIM is presented in Table 1 for four plants in the API work. Table 2 includes a summary of the operating conditions for each unit in Table 1. For the most part, PROSIM compares quite favorably with the experimental data. However, the results in Table 1 indicate a few inconsistencies that should be discussed.

Table 1. PROSIM comparison to data from API Reboiler Emissions Work Group.

Emitted Compound	**Plant Feed (tons/yr)**	**Measured Emission Rate (tons/yr)**	**PROSIM Emission Rate (tons/yr)**
Oklahoma Glycol Unit			
Benzene	3.5	0.33	0.3
Toluene	22	2.21	2.7
Ethylbenzene	1.1	0.17	0.2
Xylenes	19	1.96	5.5
Louisiana Glycol Unit 2A			
Benzene	19	0.87	1.3
Toluene	34	1.55	2.1
Ethylbenzene	3.0	0.12	0.19
Xylenes	38	1.34	2.9
Louisiana Glycol Unit 2B			
Benzene	19	3.29	4.3
Toluene	34	7.22	6.5
Ethylbenzene	3.0	0.44	0.47
Xylenes	38	5.38	6.1
Southwest Texas Glycol Unit			
Benzene	67	3.0	4.5
Toluene	92	10.9	7.8
Ethylbenzene	*	0.8	*
m,p-Xylene	24	5.1	3.4
o-Xylene	8.9	0.2	1.8

*No ethylbenzene feed data available for this unit.

Table 2. Summary of pertinent operating parameters in the API Reboiler Emissions Work Group data.

Parameter	**Oklahoma Unit**	**Louisiana Unit 2A**	**Louisiana Unit 2B**	**Southwest Texas**
Reboiler temperature (^{o}F)	354	362	362	350
Separator pressure (psia)	*	*	*	60
Separator temperature (^{o}F)	*	*	*	130
Glycol circulation rate (gal/hr)	16	14	54	62.5
Glycol circulation rate (gal TEG/lb water)	2.5	4.6	17.7	3.4
Contactor pressuire (psia)	675	960	960	990
Contactor temperature (^{o}F)	100	82	82	86
Feed rate (MMscfd)	2.2	2.3	2.3	12.7

*These facilities did not include a separator.

The xylene emissions in the Oklahoma plant were measured as 1.96 tons/yr while PROSIM predicted 5.5 tons/yr. Considering the benzene:xylene ratio in the feed, the 1.96 value would be approximately correct if the relative volatilities were approximately equal. However, xylene is significantly less volatile than benzene and should be emitted more at the regenerator since it is absorbed more in the contactor. This volatility difference is evident from the boiling point differences and the Robinson BTEX-glycol VLE data.[5] Thus the xylene emissions should likely be greater than 1.96 tons/yr.

The xylene data for the Southwest Texas unit also appears to be inconsistent. The feed for the o-xylene isomer is approximately 37% of the meta and para isomer total. However, the emissions for o-xylene are 4% of the other isomers. Intuitively, this rate should be approximately equal to the feed ratio since all xylene isomers have practically equivalent volatilities. If the total xylenes in the plant emissions are added and compared to the total xylene predictions by PROSIM, the values compare quite favorably. This may indicate that the analysis did not properly separate the isomers.

The other plants in the API work did not compare as favorably as those in Table 1 and are not presented in this paper. One notable case was the plant labeled "United States Glycol Unit" in the API report. This unit had a 52 MMscfd gas feed rate with a 270 gal/hr glycol circulation rate. The total amount of benzene, toluene, ethylbenzene, and xylenes fed to the unit was 1001, 946, 80, and 636 tons/yr, and the emission rates were 4.9, 5.6, 0.6, and 4.2 tons/yr, respectively. Since the contactor temperature was similar to that of the Southwest Texas unit, a comparison between the numbers given above and those in Tables 1 and 2 can be made. Also the contactor pressure for this plant was about 10% higher than the Southwest Texas unit. Additionally, the glycol circulation rate was 35% higher on a gallon of glycol per pound of water absorbed basis. All these factors indicate that the BTEX emissions should be 20-40 times higher than those reported by API. In fact, PROSIM predicts that the fraction of aromatics removed from the feed is approximately the same for this unit as the others investigated. Based on the above considerations, this result would be expected.

The inconsistencies in the API units can probably be attributed to the extreme difficulty in obtaining accurate information for these plants. The API cover letter indicated that due to the difficulty in performing the compositional analyses, the error could be as high as 25%. However, this does not include sample collection errors which can make the true error much higher.

ANALYSIS OF VOLATILE ORGANIC EMISSIONS FROM A TYPICAL DEHYDRATION FACILITY

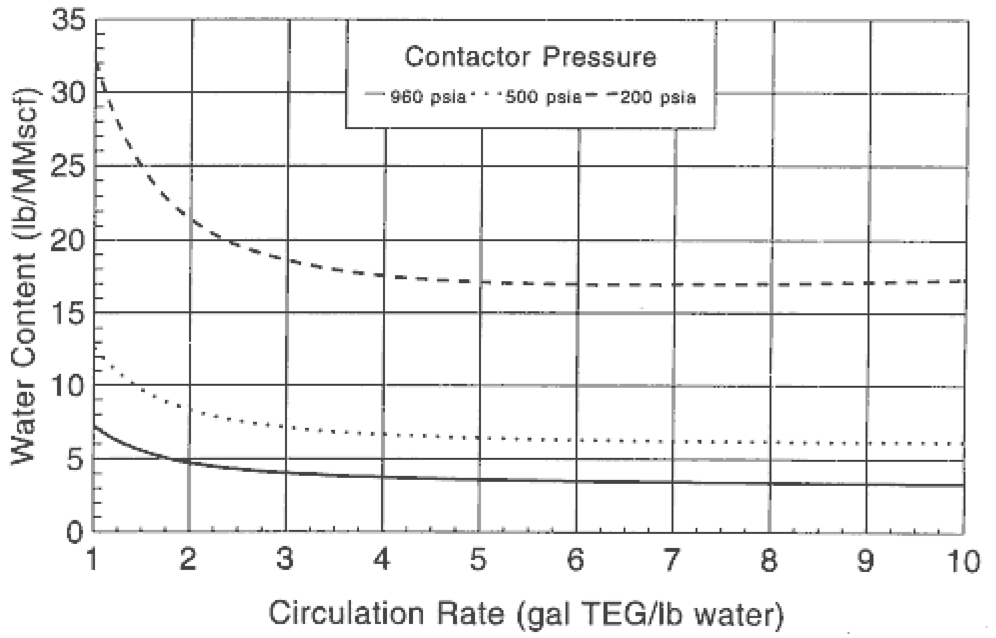
In the next section of the paper, PROSIM is used to examine non-aromatic and BTEX emissions from a typical dehydration facility at various plant configurations and operating parameters. For consistency with an actual plant, a base case similar to the API Louisiana Glycol Unit 2A was chosen. The only difference in the two units was the increase in feed flow to 30 MMscfd to illustrate emissions at medium size facilities. The conditions for this basis are presented in Table 3. The component feed rates are those into the contactor from the inlet separator, not from the well heads. A small amount of the feed (about 0.5 mole %) from the well heads is recovered as condensate in the inlet separator.

Table 3. Operating parameters of analyzed dehydration unit.

Parameter	**Value**
Contactor pressure (psia)	960
Contactor temperature (^{o}F)	82
Reboiler temperature (^{o}F)	362
Reboiler pressure (atm)	1
Feed flowrate (MMscfd)	30
Benzene feed (t/yr)	202
Toluene feed (t/yr)	276
Ethylbenzene feed (t/yr)	16
Xylene feed (t/yr)	168

A. Residual Water Content of Dry Gas

Figure 2 presents the residual water content of the dry gas leaving the contactor. In addition to the 960 psia base case, Figure 2 presents curves for contactors operating at 500 and 200 psia. The figure clearly indicates that for all these pressures, increasing the circulation rate above 3-4 gal TEG/lb water does not remove a significantly larger amount of water. This means that the gas leaving the contactor is near equilibrium with respect to water in the lean glycol at the top of the contactor. In other words, the dry gas has a water partial pressure equal to that of the water in the lean glycol. If more drying is required, the equilibrium must be shifted by changing parameters such as reboiler temperature or adding strippin gaas to the unit. Depending on the dew point depression desired, a minimum circulation rate of 3 gal TEG/lb water should likely be used to fully utilize the glycol.



TEG conc: 98.0 wt %

Figure 2. Residual water content of dry gas.

As stated earlier, the number of stages and the glycol circulation rate affect the approach to equilibrium with the lean glycol at the top of the absorber. Therefore, if fewer stages are in the absorber, this approach will be met at a higher glycol circulation rate than shown in Figure 2.

B. Non-Aromatic VOC Emissions

Figures 3 and 4 present the non-aromatic hydrocarbon emissions occurring from the dehydration unit base case at various glycol circulation rates. Also illustrated in the figures is the effect of adding a flash separator to the rich glycol between the contactor and regenerator. Several different flash tank operating temperatures are illustrated at a pressure of 75 psia. The 86, 130, and 190^{o}F temperatures are indicative of units with adiabatic separators or slight heating obtained from the reflux coil in the regenerator. The 300^{o}F temperature separator would normally be placed after the lean/rich cross exchanger. For this temperature, a 75 psia and 25 psia unit were investigated.

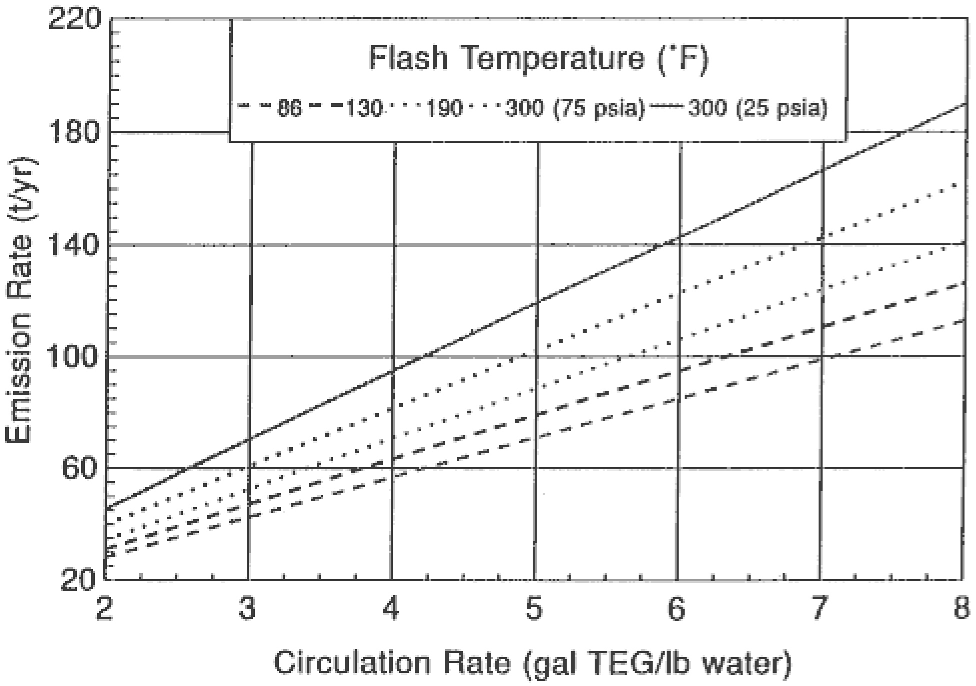
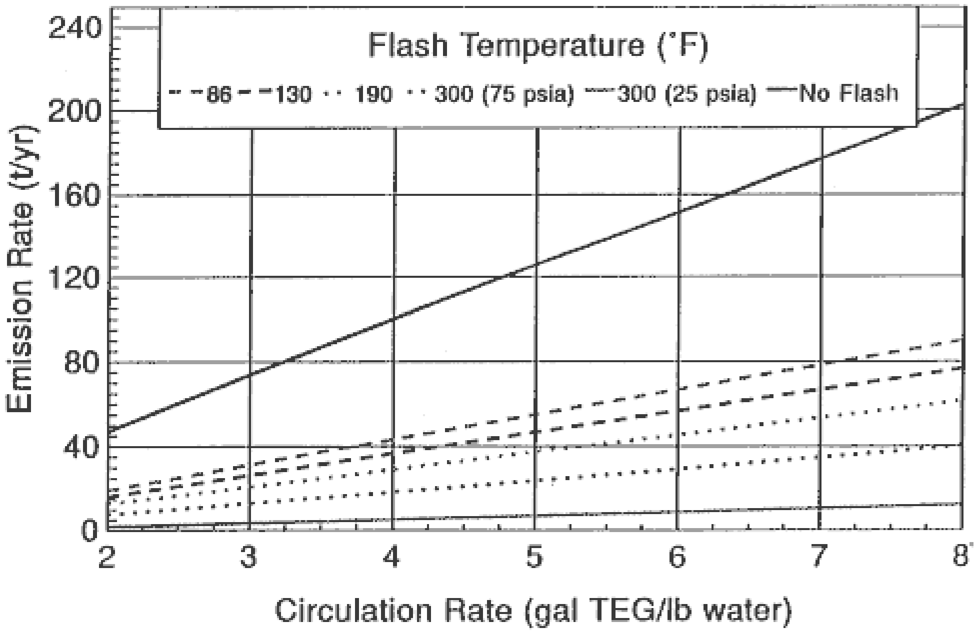


Figure 3. Non-aromatic VOC emissions from the flash tank.



Reboiler temperature: 362°F

Figure 4. Non-aromatic VOC emissions from the regenerator.

As expected, a larger fraction of the dissolved hydrocarbons are liberated in the separator with higher temperatures and lower pressures. As more are released in the separator, less are released in the regenerator. The total of the VOC emissions from the regenerator and separator is consistent for a single glycol circulation rate. This total is reflected by the no flash case in Figure 4. More than 50% of the VOC's are removed from the glycol in the separator, even for the adiabatic case. With heating to 190°F at a pressure of 75 psia, about 65% of the compounds are released.

C. Aromatic Emissions

Figures 5 and 6 present the BTEX emissions occurring from the glycol unit at various glycol circulation rates. As with the non-aromatic case, the effect of a flash separator is also included in the figures.

Contrary to the non-aromatic compounds, an insignificant fraction of the total dissolved aromatics are released in the separator at temperatures up to 190°F at 75 psia. Even in the 300°F and 25 psia separator, only about 35% of the total amount absorbed in the contactor is released at the separator.

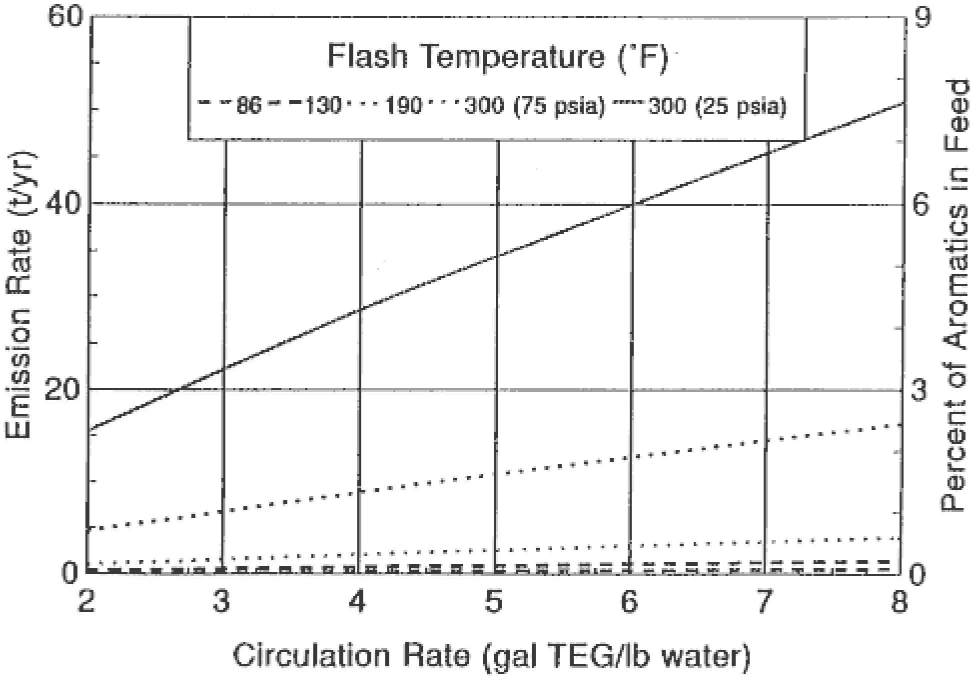
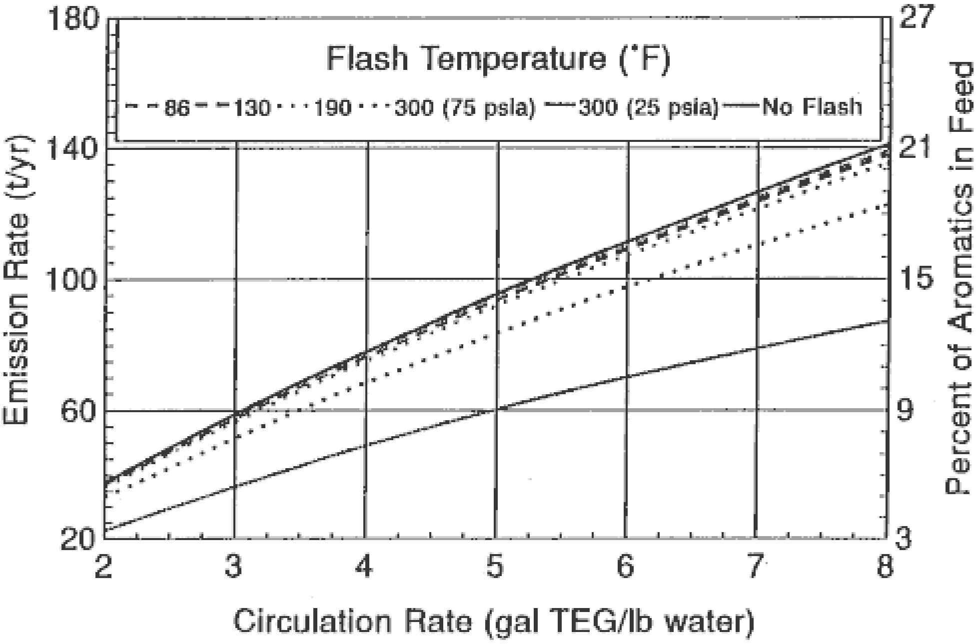


Figure 5. Aromatic emissions at the flash tank.

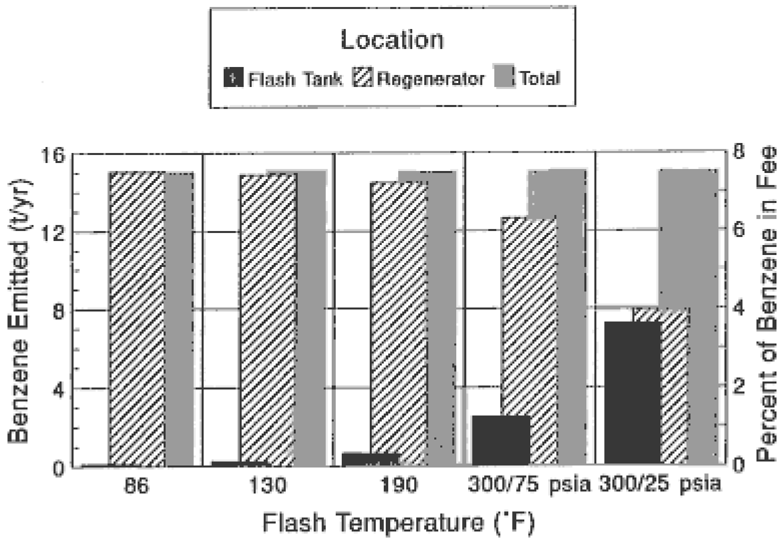


Reboiler temperature: 362°F

Figure 6. Aromatic emissions from the regenerator.

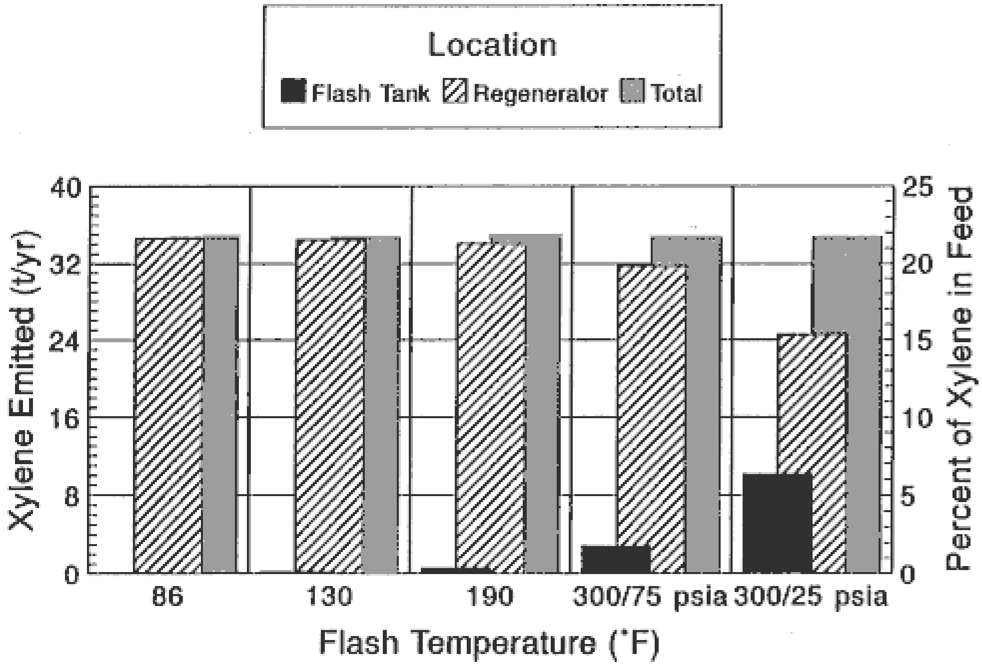
Figures 5 and 6 also indicate the fraction of the aromatics in the plant feed released in the regenerator and separator. The No Flash line of Figure 6 represents the total amount of aromatics absorbed in the contactor since only a trace amount of hydrocarbons will remain in the regenerated solution. Figures 5 and 6 also indicate another significant point. Figure 2 illustrated that the dehydrating effect is not significantly increased with circulation rates above 3-4 gal TEG/lb water. However, Figures 5 and 6 indicate that increasing the glycol circulation beyond this range will cause aromatics to be absorbed at a rate nearly proportional to the increase in circulation rate. Consequently, Louisiana Glycol Unit 2B in the API work is not dehydrating significantly more than Louisiana Unit 2A but is absorbing about four times the amount of aromatics. The unit is also circulating about four times the amount of glycol per pound of water as the 2A unit.

Figures 7 and 8 provide the emission rates for the lowest and highest boiling aromatics, benzene and xylene, at a glycol circulation rate of 3.1 gal TEG/lb water absorbed. As stated earlier, a higher fraction of the absorbed benzene than xylene is evolved from the rich glycol in the separator due to its higher volatility. Similarly, a larger fraction of the xylene is released in the regenerator. This difference in relative volatility for benzene and xylene in glycol is also apparent when Figures 7 and 8 are compared to the feed amounts presented in Table 3. For this case, the comparison indicates that about 6.5% of the benzene in the feed is absorbed compared to 19% for xylene in the contactor.



Regnerator temperature: 362^{o}F, TEG circulation: 3.1 gal/lb

Figure 7. Benzene emissions at the flash tank and regenerator.

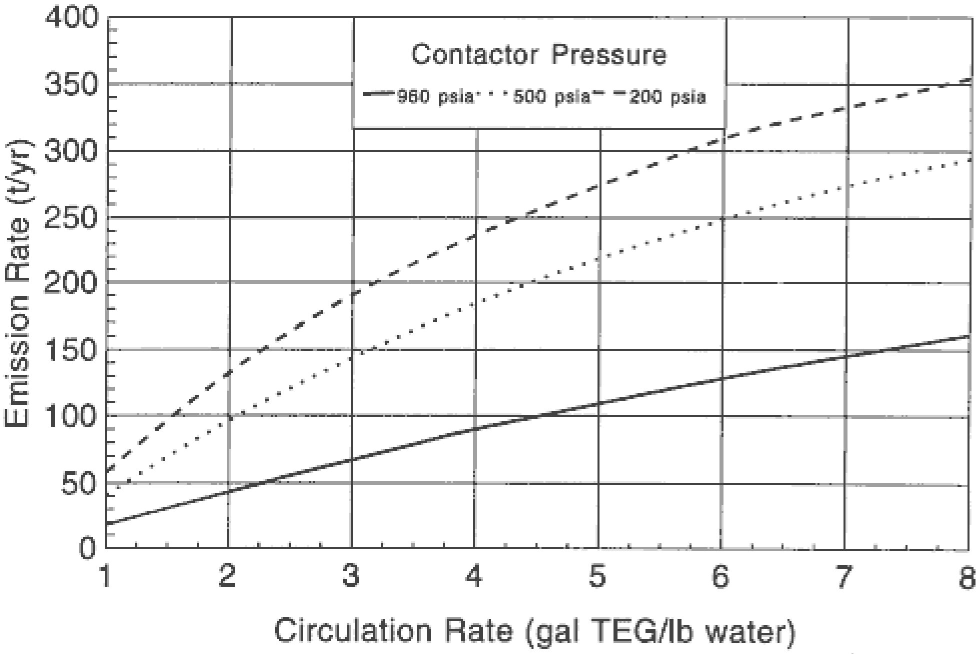


Regnerator temperature: 362^oF, TEG circulation: 3.1 gal/lb

Figure 8. Xylene emissions at the flash tank and regenerator.

EFFECT OF CONTACTOR PRESSURE ON AROMATIC EMISSIONS

Figure 9 presents the effect of contactor pressure on aromatic emissions. The figure presents the total BTEX emissions or the total amount of aromatics absorbed in the contactor. For this work, pressures of 960, 500, and 200 psia were chosen to represent high, medium, and low pressure units, respectively. All other conditions are the same as used in the earlier cases.



Gas temperature: 82^oF

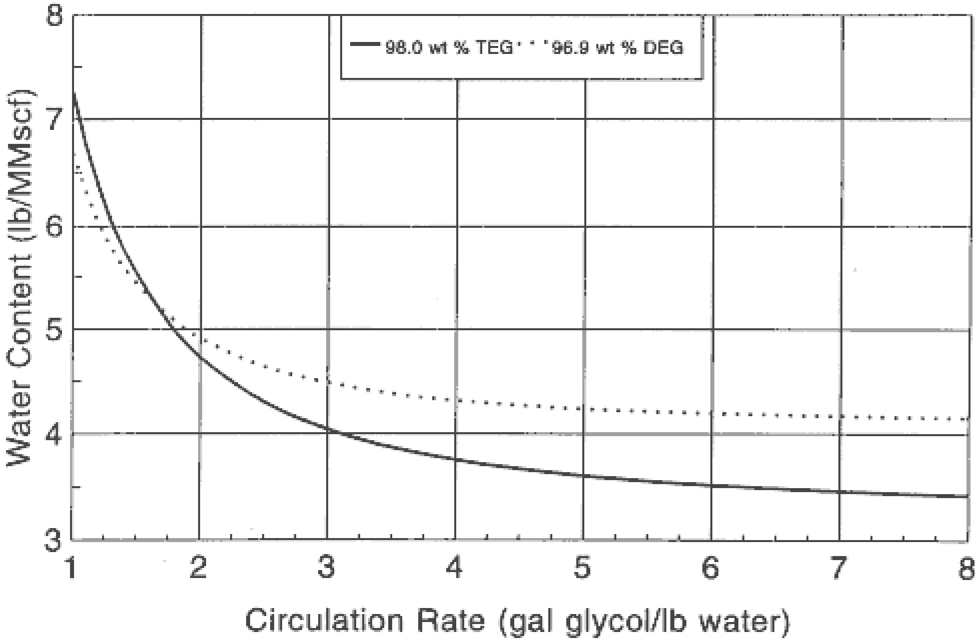
Figure 9. Contactor pressure effect on total aromatic emissions.

Figure 2 indicates that in the three contactor pressures, equilibrium with respect to water in the lean glycol is approached with circulation rates in excess of 3 gal TEG/lb water absorbed. The 200 psia unit indicates that as circulation is increased above about 7 gal/lb, the residual water content begins to increase slowly for this pressure. At high circulation rates, the temperature within the contactor begins to increase due to the larger amount of glycol (at the trim cooler or gas/glycol exchanger temeprature) relative to the gas. If the duty of the trim cooler or gas/glycol exchanger is limited, this increase will be sharper or occur at lower circulation rates since the lean glycol cannot be cooled to the proper temperature. Further, the lower pressure unit will have to absorb more water vapor causing an increased contactor temperature from the heat of absorption.

As expected, vapor-liquid equilibrium data show that BTEX compounds are more soluble in glycols at higher pressures. However, increased water content in low pressure gas requires a larger circulation rate to be used. This higher circulation results in the higher aromatic emissions illustrated in Figure 9. Additionally, the low pressure facilities will emit more non-aromatic VOCs for the same reasons.

COMPARISON OF AROMATIC EMISSIONS USING TEG AND DEG

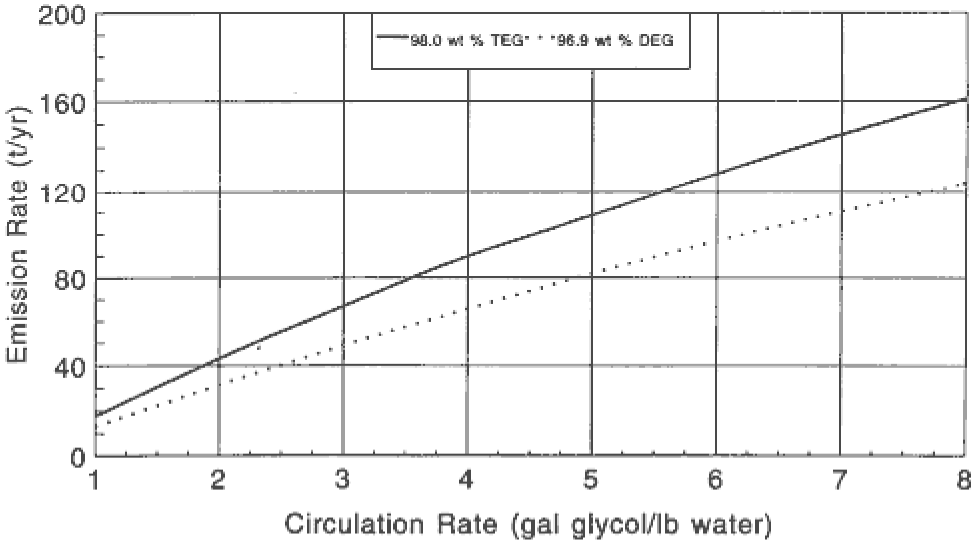
For this final section, the total BTEX emissions from a DEG unit are compared to those from a TEG unit. The comparison is made from the 960 psia basede unit. Figure 10 presents the residual water content similar to Figure 2, but now includes DEG. As with TEG, equilibrium with respect to water is approached at circulation rates on the order of 3-4 gal/lb for DEG. However, TEG provides slightly better desiccation properties since it can be regenerated to a higher concentration. Vaporization losses occur to a greater extent when DEG is regenerated to high purity without special design.



Gas temperature: 82^{o}F

Figure 10. Residual water content of dry gas using DEG and TEG.

Figure 11 compares the total BTEX emissions for DEG and TEG dehydration. Due to increased solubility in TEG, higher emissions occur when using TEG. From the figure, this increase amounts to approximately 30-40% more than the DEG unit. As with TEG, the emissions increase linearly with glycol circulation rate so that circulation above 4 gal/lb will result in higher emissions without greater dehydration.



Gas temperature: 82^{o}F

Figure 11. Total aromatic emissions for DEG and TEG units.

SUMMARY

In this paper, a general purpose process simulator known as PROSIM was used to model the emissions from glycol dehydration facilities. PROSIM was shown to adequately represent data from the API Glycol Emissions Work Group. The program indicated that a majority of non-aromatic emissions are released at the flash separator in dehydration units. However, only a small fraction of BTEX emissions are released in the separator, except at high temperature (> 300^{o}F) and low pressure. An analysis of operation at three different contactor pressures revealed that even though hydrocarbons are more soluble in glycol at higher pressures, a larger amount is emitted in low pressure units due to the larger circulation rate required to remove a larger amount of water. The program predicts that TEG units circulating the same quantity of glycol on a per pound of water absorbed basis will absorb about 30-40% more BTEX components than DEG units. In all cases, the model indicates that over-circulation of glycol does not enhance dew point depression but will greatly increase hydrocarbon absorption in the contactor, including BTEX compounds.

REFERENCES

1. Kohl, A. and Riesenfeld, F., *Gas Purification,* Gulf Publishing Co., Houston. 1985.

2. Fitz, C. W., and Hubbard, R. A., "Quick, manual calculation estimates amount of benzene absorbed in glycol dehydrator," *Oil & Gas J.,* Nov. 23, 1987, p. 72.

3. API Glycol Reboiler Emissions Measurement Work Group, Progress Report April 7, 1992, and June 19, 1992, furnished by Vernon H. Schievelbein, Texaco E&P Technology Department.

4. Gas Processors Suppliers Association, *Engineering Data Book,* 1987.

5. "The Solubility of Selected Aromatic Hydrocarbons in Triethylene Glycol," D. B. Robinson Research LTD., *GPA Research Report RR-131,* Gas Processors Association, Tulsa, Oklahoma, December, 1991.