An Analysis of BTEX emissions from Amine Sweetening and Glycol Dehydration Facilities

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ABSTRACT

The amount of BTEX components emitted from gas processing facilities has become a significant environmental concern. Recently, amine sweetening units have received the same environmental scrutiny as glycol units with regard to BTEX emissions. This paper compares the BTEX emissions from amine sweetening and glycol dehydration facilities as well as the methods available to minimize BTEX pickup in these systems. Reducing solvent circulation rates in both the amine and glycol units and minimizing the lean amine temperature were found to be the most effective ways of limiting overall BTEX emissions. Changing solvent type can also reduce emissions, but the effect on treated gas quality must be considered as well. In the cases investigated approximately 25% of the overall BTEX emissions came from the amine units, while the remaining 75% came from the glycol system.

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INTRODUCTION AND BACKGROUND

In 1990 several new regulatory programs were established under the Clean Air Act Amendments that changed the way gas processors viewed their plants. Several aromatic compounds including benzene, toluene, ethylbenzene and xylene, collectively known as BTEX, were included on a list of 189 hazardous air pollutants (HAP). The limits placed on these compounds are 25 tons per year (tpy) of total BTEX and no more than 10 tpy of any individual compound[1,2]. Previously, producers had known that some level of BTEX existed in a number of natural gas streams, but they had not bothered to test for these components. Special procedures were necessary, and the amounts in question were typically on a part per million basis.[3]

The industry has given increased attention to these compounds, and in mid-1990 the Gas Processors Association (GPA) and American Petroleum Institute (API) got involved with the issue. In the late 1980's, GPA and API had jointly funded a research project to investigate the solubility of light hydrocarbons in water and in desiccant systems. Due to the new regulations, the project focus was shifted to evaluating the solubility of the BTEX compounds in triethylene glycol (TEG) solutions instead. The results from this work were published in GPA Research Report RR-131.[4]

Additional information was gathered by the API Glycol Reboiler Emissions Measurement Work Group who collected field data on BTEX emissions from ten operating plants in Oklahoma, Louisiana and Texas. The information was then provided to several companies for the purpose of developing computer models to estimate the BTEX emissions from glycol unit regenerators.[3] Bryan Research & Engineering included information from both the GPA and API research along with plant data in the process simulator PROSIM®[5]. Results from PROSIM have been evaluated against data taken from the operating plants and found to compare favorably as shown by Hlavinka, et al[6,7].

Since these early studies were initiated, research projects in the area have been increasing. Radian Corporation has performed several studies in conjunction with GPA and the Gas Research Institute (GRI). Much of the research involves developing simple, yet accurate analytical methods to measure the BTEX content of vent gas streams. These methods include direct measurement and indirect measurement by rich/lean glycol material balance (LRGCC 1993)[8].

Recently, BTEX emissions from amine treating units have also been targeted, and consequently attention is being given to reducing these emissions as well[9]. GRI has also sponsored research in this area, and results from some of this work were presented at the 1995 GRI Glycol Dehydrator/Gas Processing Air Toxics Conference in Denver[10]. A more in depth report was published in early 1996[11]. Bryan Research & Engineering used this data to incorporate the BTEX components into its amine process simulator, TSWEET®[12]. Comparison of TSWEET predictions to operating data by Morrow and Lunsford[9] has shown good results.

This paper examines the influences of various plant operating parameters for both amine sweetening and glycol dehydration units on BTEX emissions using TSWEET and PROSIM. All figures and tables were developed from the results obtained using these programs.

INTEGRATED GAS PLANT CONFIGURATION

Figure 1 shows a process flow diagram for a typical gas processing facility containing an amine treating unit for H_2S and/or CO_2 removal and a glycol dehydration unit for water removal. If the raw gas contains appreciable amounts of H_2S, a sulfur plant or other sulfur reduction method is used to treat the overheads from the rich amine stripper. This treating normally destroys any BTEX or other hydrocarbons. However, if little or no H_2S is present, this gas may be vented directly to the atmosphere, and BTEX emissions may be of concern. Limiting the BTEX entering a sulfur plant is also advantageous since these compounds can hurt overall sulfur recovery[13,14,15].

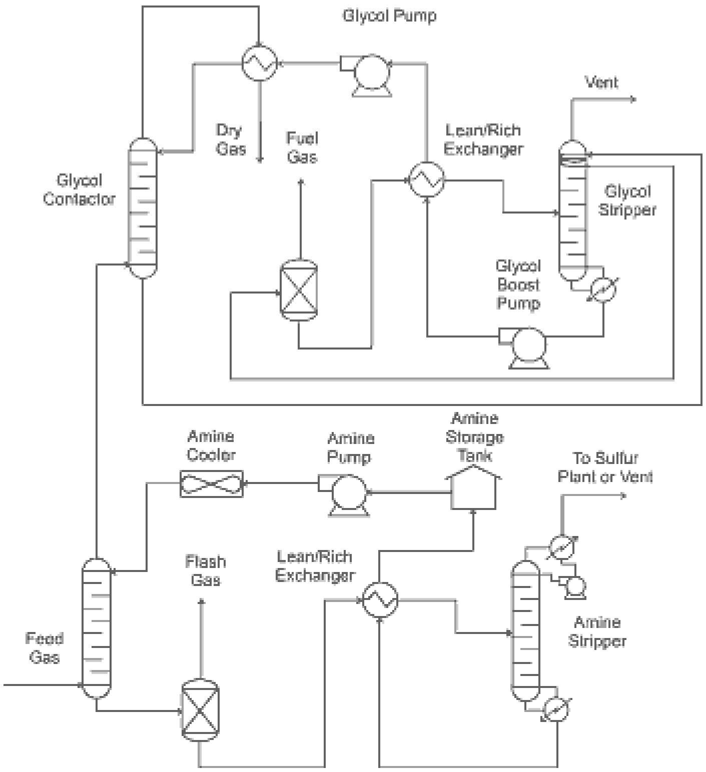

Figure 1. Integrated Gas Processing Plant

AMINE PLANT OPERATION

An amine unit operates by contacting an alkanolamine solution with the sour gas (or liquid) feed countercurrently in an absorber column. H_2S and CO_2 in the feed are absorbed by the amine in the solution, and the sweetened gas exits the top of the column. Rich amine exits the bottom of the column and is sent through a regeneration system to remove the acid gases and dissolved hydrocarbons, including BTEX. The lean solution is then recirculated to the top of the absorber to continue the cycle. The sweetened gas exiting the absorber is saturated by water from its contact with the amine and must be dehydrated before being processed further or sent to a pipeline. The overheads from the amine regenerator column are sent to a sulfur recovery unit or vented to the atmosphere depending on the sulfur content.

Operating Parameters

Several operating parameters directly affect the amount of BTEX absorbed in an amine unit. These factors include the inlet BTEX composition, contactor operating pressure, amine circulation rate, solvent type and lean solvent temperature. Table 1 shows the process conditions used to investigate the effects of some of these parameters on BTEX pickup. Figures 2 and 3 show the BTEX emission rates predicted by TSWEET for MEA, DEA and MDEA as functions of circulation rate and lean solvent temperature.

Table 1. Amine Unit Base Case Parameters

Inlet Gas

Temperature F	Pressure psia	Flowrate MMSCFD
90	1000	50

Component	Composition Mol %	Component	Composition Mol %
H2O	0.10	IC4	0.40
N2	0.50	C4	0.50

CO2	7.00	IC5	0.20
C1	84.45	C5	0.15
C2	4.60	C6	0.21
C3	1.70	C7+	0.15

Component	Benzene	Toluene	Ethylbenzene	O-Xylene
ppm	200	170	10	90

Process Equipment

Contactor	Flash	L/R Exchanger	Stripper	Pump	Cooler
7 ideal stages	75 psia	200 F	10 ideal stages	1000 psia	120 F
6 ft. diameter		rich outlet	28 psia ovhd.		
3 in. weir		temperature	120 F cond. temp.		
			1.0 lb steam/gal sol.		

Amine Strengths

Amine	MEA	DEA	MDEA
Wt. %	20	30	50

Note: A circulation rate of 600 gpm amine is used unless otherwise noted.

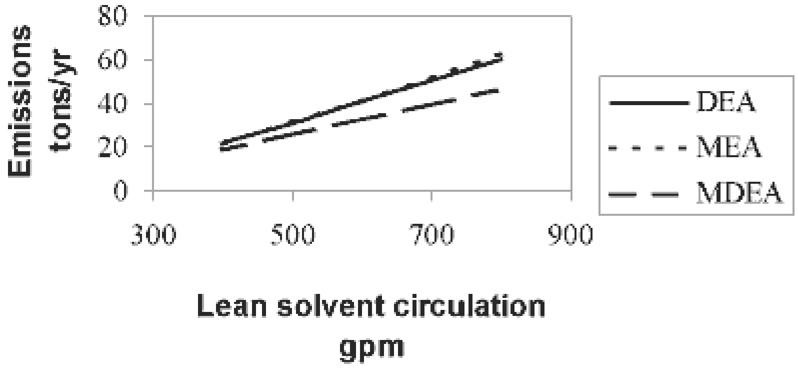

Figure 2. BTEX Emissions vs. Lean Amine Circulation

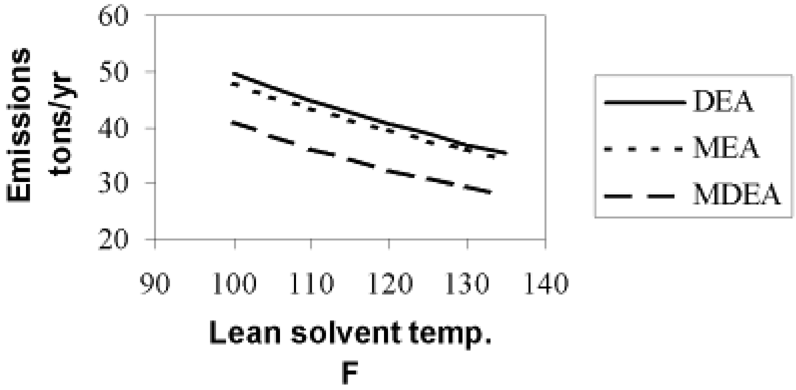

Figure 3. BTEX Emissions vs. Lean Amine Temperature

A. Amine Circulation Rate

Figure 2 illustrates the dependence of BTEX emissions in an amine unit on the lean solvent circulation rate. As the circulation increases, so do the BTEX emissions. The BTEX emissions equate to approximately 2-6% of BTEX in the inlet gas. While minimizing the circulation rate in any amine unit makes sense from an economic standpoint, it is crucial to limiting the amount of BTEX absorbed.

B. Lean Solvent Temperature

Figure 3 shows that the amount of BTEX emissions in amine systems decreases with an increase in lean solvent temperatures. However, increasing the lean solvent temperature also decreases the pickup of H_2S and results in higher circulation rates and/or higher reboiler duties to make specification. CO_2 pickup will also decrease in MEA and DEA; although, it may actually increase under certain conditions using MDEA. Figure 4 also shows that the amount of water in the sweetened gas increases dramatically with increased lean solvent temperature, and thus results in a larger load on the downstream glycol system, which would in turn increase its BTEX emissions.

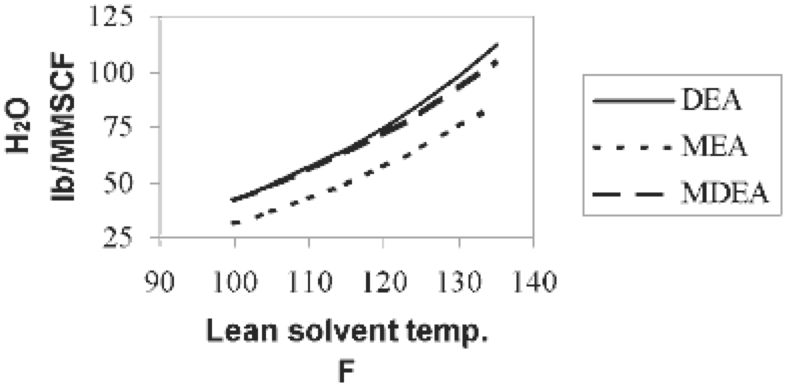

Figure 4. Water in Sweetened Gas vs. Lean Amine Temperature

C. Amine Type

As seen on both Figures 2 and 3, MDEA absorbs the lowest amount of BTEX, and MEA has only slightly increased emissions over DEA for the same circulation rates and at the same lean solvent temperatures. Although this would suggest that MDEA should always be used over the other two amines from an emissions standpoint, the CO_2 and H_2S specification in the sweet gas must also be taken into account. At lower pressures MDEA may be unable to achieve a very low specification for either component[16].

GLYCOL PLANT OPERATION

Once the saturated sweetened gas leaves the amine unit, it must be dehydrated, typically with a glycol system, before further processing can take place. The operation of a glycol unit is very similar to that of an amine unit. In a standard glycol unit the wet gas is contacted countercurrently with lean glycol in an absorber column. Water in the gas is absorbed into the glycol, and the dry gas exits the top of the column. Rich glycol exits the bottom of the column and is sent through a regeneration system to remove the excess water. Any dissolved hydrocarbons, including BTEX, leave the system as vent gas in the regenerator or as flash gas. The regenerated glycol is then cooled and recycled back to the top of the absorber column.

Operating Parameters

The effect of operating parameters on BTEX emissions from glycol dehydration facilities has been comprehensively presented earlier[7]. However, for convenience and development of the current scenario, a brief analysis is provided here.

Again, the same parameters that affect BTEX absorption in amine units also apply to glycol units. Lean solvent circulation rate and lean solvent temperature are potential process variables in determining BTEX pickup. One other factor to consider is the stripper pressure which has a large effect on the lean glycol water content. Table 2 shows the process conditions used to investigate the effect of these parameters on BTEX emissions from glycol units. It should be noted that the cases investigated have been simplified to show the effects of a single variable on BTEX emissions. The dehydrated gas in each case may not necessarily pass pipeline specifications.

Table 2. Glycol Unit Base Case Parameters

Inlet Gas

Temperature F	Pressure psia	Flowrate MMSCFD
120	1000	47

Component	Composition Mol %	Component	Composition Mol %
H2O	0.22	IC4	0.43
N2	0.41	C4	0.53
CO2	1.86	IC5	0.21
C1	89.54	C5	0.16
C2	4.69	C6	0.22
C3	1.61	C7+	0.16

Component	Benzene	Toluene	Ethylbenzene	O-Xylene
ppm	215	180	100	95

Process Equipment

Contactor	Flash	L/R Exchanger	Stripper	Pump	Cooler
2 ideal stages	75 psia	300 F (TEG) 250 F (DEG) rich outlet temperature	4 ideal stages 14.7 psia ovhd. 0.2 reflux ratio 400 F (TEG), 320 F (DEG) reboiler temperature	1000 psia	120 F

Note: A glycol circulation rate of 4 gal./lb. H2O is used unless otherwise noted.

A. Lean Solvent Circulation Rate

As with the amine systems, BTEX emissions from a glycol unit are strongly dependent upon the circulation rate. Figure 5 shows that BTEX pickup increases almost linearly with an increase in circulation rate. However, Figure 6 shows that there is very little benefit in circulating more than four gallons of solvent per pound of water in the inlet gas. Again, from an economic point of view and to limit BTEX emissions, minimization of solvent circulation is crucial.

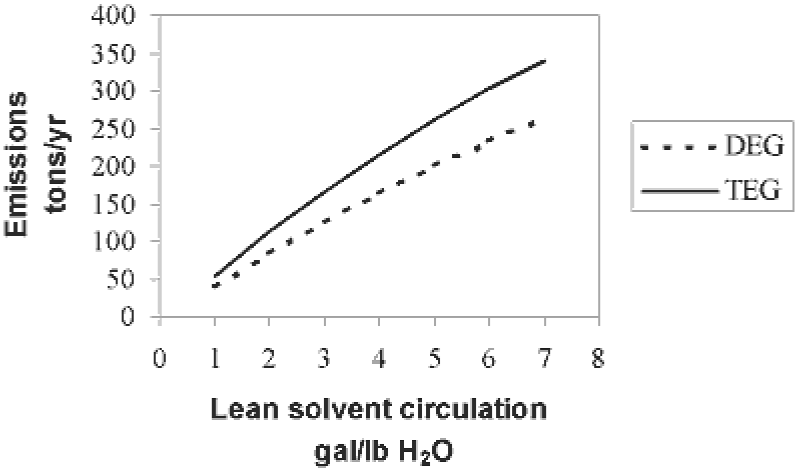

Figure 5. BTEX Emissions vs. Lean Glycol Circulation

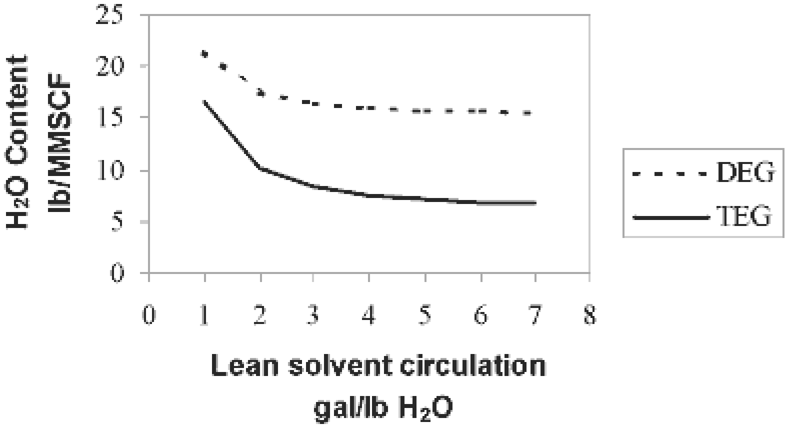

Figure 6. Residual Water Content vs. Lean Glycol Circulation

B. Lean Solvent Temperature

As shown in Figure 7, the lean glycol temperature has very little effect on the BTEX emissions from a dehydration unit. This notable difference from BTEX absorption in amine units is due to the relatively large gas to glycol mass ratio, approximately 13:1 in the cases presented here. As a result, the rich glycol temperature is primarily a function of the inlet gas temperature. In an amine unit the gas to amine mass ratio is typically much lower, approximately 1:3 in the cases presented here, and the treated gas temperature is normally within a few degrees of the lean amine temperature. Figure 8 shows that the water content of the treated gas is only weakly related to lean glycol temperature as well.

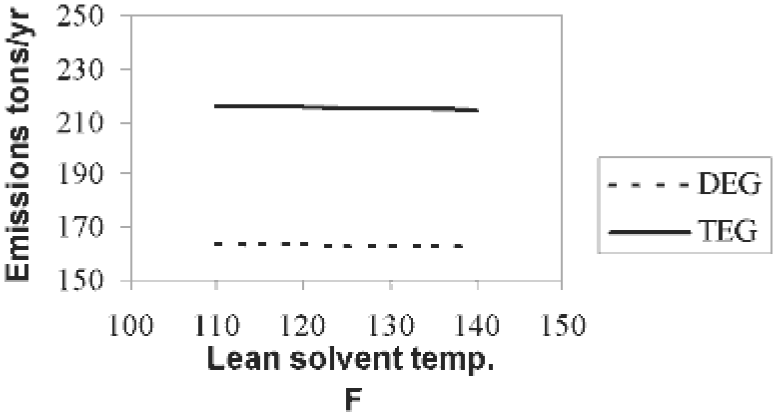

Figure 7. BTEX Emissions vs. Lean Glycol Temperature

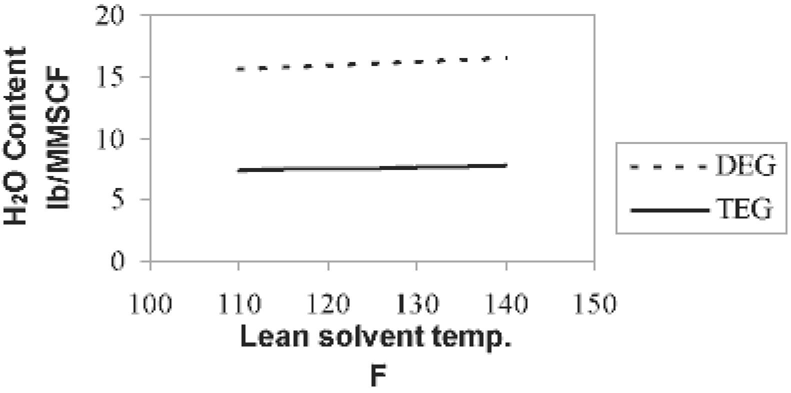

Figure 8 – Residual Water Content vs. Lean Glycol Temperature

C. Stripper Pressure

Another process parameter that can have affect the BTEX emissions from a glycol unit is the stripper pressure. As seen in Figure 9, the higher the stripper pressure, the lower the overall BTEX emissions. This is due to a change in the equilibrium composition in the stripper, and the effect is more noticeable with DEG than with TEG. However, increasing the stripper pressure also increases the water in the lean solvent and may mean that the water specification cannot be met in the treated gas without using stripping gas. Thus the potential decrease in BTEX emissions at higher stripper pressures may be outweighed by the pipeline requirements. Figure 10 illustrates this limitation.

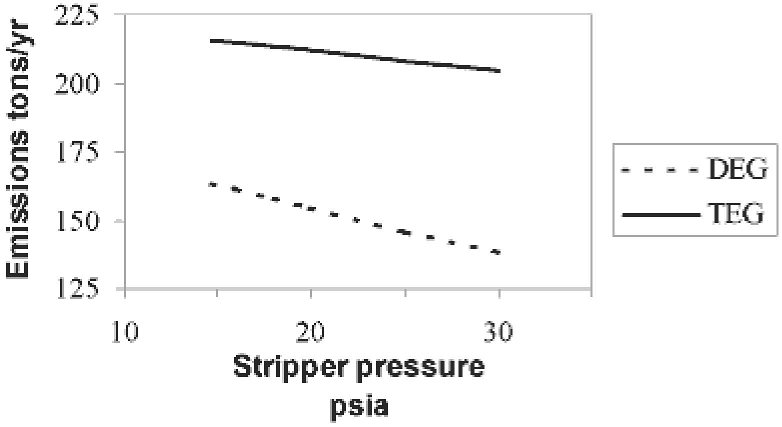

Figure 9. BTEX Emissions vs. Glycol Stripper Pressure

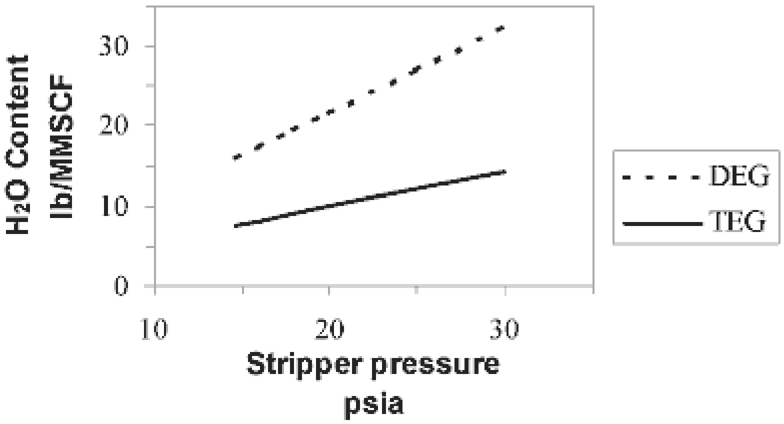

Figure 10. Residual Water Content vs. Glycol Stripper Pressure

D. Glycol Type

Two facts are clear based on all of the preceding figures:

1. There are fewer BTEX emissions from a given DEG unit than a comparable TEG unit at the same operating conditions.
2. DEG units cannot treat a wet gas to the same level as a TEG unit at the same circulation rate.

The solvent choice for a given situation must consider both of these factors. If the treated gas water specification is sufficiently low, DEG may be unable to accomplish the job and may be ruled out regardless of the emissions benefits.

MINIMIZATION OF TOTAL EMISSIONS

In an integrated plant with both amine and glycol units, the ultimate goal is to limit total BTEX emissions. By comparing Figures 2 and 3 with Figures 5, 7 and 9, it is clear that the bulk of the BTEX is emitted from the glycol units. In our examples, approximately 25 % of the overall emissions are from the amine units, although the amine circulation rate is roughly *sixty* times the glycol circulation rate. This extreme difference is primarily due to the fact that the amine solutions are 85-90% water on a molar basis, whereas the glycols contain only 10-20 % water, and all of the BTEX compounds are much more soluble in glycol than in water. Therefore, it should be evident that glycol circulation rate is the most important variable that has been discussed thus far. However, the other process parameters should not be overlooked.

The following is a list of strategies that should be followed to limit BTEX emissions from an integrated gas plant:

1. Minimize the lean amine circulation rate. BTEX emissions are directly proportional to the circulation rate.
2. Minimize the lean amine temperature. This parameter has a significant effect on the amount of water fed to the glycol unit, and thus the amount of glycol that must be circulated to achieve a residual water specification.
3. Minimize the lean glycol circulation rate. As stated earlier, BTEX pickup in the absorber is strongly dependent on circulation rate, and circulation rates greater than 3-4 gallons per pound of water result in little decrease in outlet water content[7].

The choice of amine solvent must be weighed against items 1 and 2 above, as well as the treating requirements. At similar circulation rates, using MEA instead of DEA or MDEA reduces the amount of water in the sweetened gas. However, BTEX emissions from an MDEA unit and the associated glycol system under the same conditions are considerably lower. The choice of dehydration solvent in a glycol system must be weighed against treating requirements also. If a DEG system can achieve the required water removal, then it should be used instead of TEG to limit BTEX emissions.

From the discussion above, it is clear that a number of factors need to be examined when designing a grass-roots gas processing facility. The amine unit must meet the required sweet gas specification, but the potential environmental consequences (i.e. BTEX emissions) should also be considered. Lean amine temperature, lean solvent circulation rate and solvent selection all factor into the final operation of the plant. Similar parameters need to be addressed in the design of the glycol dehydration system, and in which BTEX emissions are even more important. Given the number of parameters that need to be addressed, a thorough parametric study should be performed to maximize operating efficiency while minimizing BTEX and other emissions.

OTHER OPTIONS TO CONSIDER

Once all of the strategies on the previous list have been investigated and optimized, the overall BTEX emissions may still be above the maximum limits. If such is the case, there are additional processing options that may be investigated. BTEX condensers are used to condense the aromatics from the vent gas from glycol strippers[17,18,19]. As discussed by Morrow and Lunsford, carbon beds may be used to adsorb the BTEX components in amine unit vent gas, or the vent gas may be incinerated. There are also BTEX stripper designs that use stripping gas to remove BTEX from the rich amine and glycol solutions prior to regeneration[9]. The byproduct gas is burned as plant fuel.

CONCLUSIONS

Due to growing environmental concerns, limiting the total BTEX emissions from gas processing plants is of primary importance. Glycol units have been under scrutiny for some time; however, amine units have recently been targeted as well. In the cases discussed earlier, approximately 25% of the overall emissions came from the amine units while 75% came from the glycol dehydration unit. Reducing circulation rates in both amine and glycol units and minimizing the lean amine temperature are the best ways to achieve this goal. The choice of solvent can also affect the BTEX emissions. However, treated gas specifications must be taken into account since changing operating parameters to decrease BTEX emissions can also decrease unit performance. A thorough parametric study is recommended to limit BTEX emissions while maintaining treated gas quality.

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