Recent GPA Data Improves BTEX Predictions for Amine Sweetening Facilities

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ABSTRACT

Amine solutions absorb some amount of hydrocarbons and BTEX. These dissolved hydrocarbons that are obtained by contacting with the feed gas are ultimately released in the overhead of the regenerator. This overhead either vents to the atmosphere or feeds a sulfur recovery unit. Hydrocarbon content for regenerator vents discharging to the atmosphere must comply with recent stringent regulations. For acid gas feeds to a Claus unit, excessive hydrocarbons may result in catalyst fouling, sub-quality sulfur product, or more sophisticated burner design.

To better understand and quantify hydrocarbon and BTEX solubility in aqueous amines, the Gas Processors Association commissioned research Project 971. Preliminary results from this project have been used to improve models for hydrocarbon and BTEX solubility predictions. Model predictions are compared with operating facilities and guidelines for minimizing hydrocarbon absorption in amine facilities are presented.

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INTRODUCTION

Recently there has been increased interest in BTEX (benzene, toluene, ethylbenzene and xylene) and other hydrocarbon (HC) components dissolved in aqueous amine solvents. These compounds are absorbed in the solvent when contacted with the incoming gas and then rejected in the overhead of the regenerator. If the overhead of the regenerator is vented to the atmosphere, these HC emissions are more closely regulated. If the overhead of the regenerator is fed to a burner such as in a Claus plant, the BTEX components are more difficult to destroy relative to other HCs. These BTEX components tend to deactivate the Claus catalysts, severely limiting the catalyst life.

Figure 1 shows a typical amine sweetening facility. Hydrogen sulfide and carbon dioxide and some HCs are absorbed by the amine solution in the contactor. Some of the HCs are removed in the rich flash by pressure reduction. The solvent is regenerated and the acid gas and HCs are rejected to the overhead stream. A small portion of the acid gas remains in the lean amine from the bottom of the stripper. This simple flow sheet becomes more complicated depending on the process application and product specifications. Additional draws can remove semi-lean amine from the regenerator, and side coolers may be attached to the absorber to remove heat of absorption. The lean rich exchanger can be removed entirely. For this simple amine facility, absorbed HCs can only be rejected in the rich flash or the acid gas exiting the regenerator. If HCs are not removed in the rich flash to an acceptable level before the regenerator, other process modifications must be made. For more complicated cases, the potential locations for HC rejection need to be identified.
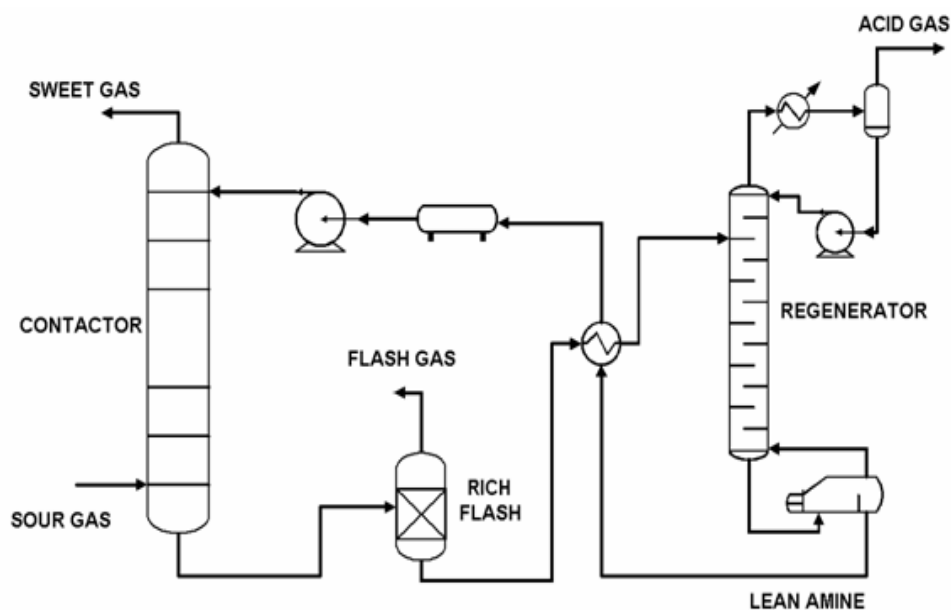
Figure 1- Simple Amine Sweetening Facility

Equilibrium Data and Modeling

Table I shows the literature sources for the solubility of light paraffins in aqueous amine solutions. The streams processed by amine sweetening units contain a high concentration of light HCs. The initial concern with HC absorption was based on product loss. Therefore most of the solubility data are for methane, ethane, and propane.   Recently, Critchfield *et al.* [9] report on the solubility of *n*-pentane in aqueous amines. Overall trends for HC solubility in amines in the operating range of a typical absorber can be summarized: increasing amine concentration increases HC solubility, increasing pressure increases HC solubility, and increasing temperature decreases HC solubility. The type of amine also influences HC solubility. MEA generally shows the lowest HC solubility followed by DEA, TEA, and then DGA^O, MDEA and DIPA, with DIPA having the greatest affinity for HCs relative to the other amines [9]. These recent findings are somewhat contradictory to the current industry doctrines.

Table I – Published Light Paraffin Equilibrium Solubility Data in Aqueous Amine Solutions

Year	Authors	Solvent	Concentration	Paraffins	Temperature
1976	Lawson and Garst [1][a]	MEA, DEA	5, 15, 25, 40 wt%	Methane, Ethane	100 – 250°F
1986	Dingman [3]	DGA	50 wt%	Methane	150 – 190°F
1992	Carroll *et al.* [4]	MDEA	3 M	Propane	25 – 150°C
1996	Jou *et al.* [5]	MDEA	3 M	*n*-Butane	25 – 125°C
1996	Jou *et al.* [6]	TEA	2, 3, 5 M	Ethane	25 – 150°C
1998	Jou *et al.* [7]	DGA	3, 6 M	Methane	25 – 125°C
1998	Jou *et al.* [8]	MDEA	3 M	Methane, Ethane	25 – 130°C
2001	Critchfield *et al.* [9]	MEA, DEA, DGA	3, 4.5 M	Methane, Ethane	40°C

MDEA, DIPA	Propane, *n*-Butane *n*-Pentane

[a] Addendum in 1996 by Mather and Marsh [2].

In contrast to the eight articles that report on HC absorption in amines, Table II lists only three papers which provide data for BTEX solubility in amines. Hagerty and Hawthorn [10] report data for benzene and toluene in MDEA and DGA solutions. Critchfield *et al.* [9] compares benzene solubility in MEA, DEA, DGA, MDEA and DIPA. Again, contrary to popular belief, the data show DIPA has a greater affinity for benzene than either MDEA or DGA. DGA showed similar affinity for benzene as MDEA. Table II also lists the highly anticipated yet unpublished results from GPA project 971 [11]. From the little published data for aromatics in amines, the overall trends of BTEX solubility appear to be similar to that of HC solubility: increasing amine concentration increases BTEX solubility, increasing pressure increases BTEX solubility, and increasing temperature decreases BTEX solubility.

Table II – Published BTEX Equilibrium Solubility Data in Aqueous Amine Solutions

Year	Authors	Solvent	Concentration	Aromatics	Temperature
1999	Hagerty and Hawthorne [10]	MDEA	25, 50 wt%	Benzene, Toluene	25 - 120°C
		DGA	35 wt%	Benzene, Toluene	60°C
2001	Critchfield *et al.* [9]	MEA, DEA, DGA MDEA, DIPA	3, 4.5 M	Benzene	40°C
To be Published	Valtz *et al.* [11]	MDEA, DGA, DEA, MEA	Varying	Benzene, Toluene, Ethylbenzene, Xylene	Varying

The solubility of other components in amine solutions and hydrocarbons in water is also available. Sada *et al.* [12,13] measured ethylene and acetylene solubility in several different aqueous amine solutions. Data were also taken for nitrous oxide. Although these data are beneficial, the primary focus of the research was to relate the solubility and diffusivity of non-reactive components with that of CO_2. Dingman [3] measured the solubility of hydrogen in solutions of MEA and DGA. Since aqueous amine solutions are primarily water, the HC and BTEX solubility in water is extremely important. Fortunately, these data are readily available in the API Technical Data Book [14] or the Solubility Data Series by IUPAC [15]. Without this water data it would be virtually impossible to develop any models for amine HC absorption.

Amine solutions absorb acid gas. This absorption can dramatically change the characteristics of the solvent. Fortunately, HC solubility in loaded amine solutions have been measured. Lawson and Garst [1] report on the solubility of methane and ethane in loaded solutions of MEA and DEA. Kohl and Nielsen [16] provide a figure to estimate the solubility of methane in loaded solutions of MEA. Dingman [3] reports data on methane and hydrogen solubility in loaded solutions of MEA and DGA. Recently, Jou *et al.* [17,18] published data for methane solubility in loaded solutions of DEA and MDEA in the presence of mercaptans. Based on the data, acid gas loading of the amine solution tends to decrease HC absorption. The magnitude of this decrease can be as much as 50% for methane [17,18]; however, additional data are required to confirm the magnitude for heavier HCs and BTEX.

In 1997, Carroll *et al.* [19] proposed a model for the solubility of light HCs in aqueous amine solutions. The model is based on a water-hydrocarbon system and uses a "salting-in" ratio to adjust the hydrocarbon Henrys constant. The salting-in ratio is expressed as a constant multiplied by the amine concentration. The constant is a function

of temperature, amine type, and the particular hydrocarbon. Carroll *et al*. [20] provide calculated results from the model for methane in MEA, DEA, DGA, and MDEA and ethane and propane in MDEA. Hagerty and Hawthorne [10] suggest another technique for modeling HC and BTEX solubility in amines, the use of an equation of state.

The vast majority of references presented in Table I and II and previously discussed are the result of very few researchers. The gas processing industry is indebted to these scientists for the tremendous amount of work they have contributed.

PUBLISHED Operating Data

Amine HC and BTEX Absorption

A literature review of amine sweetening units with reported HC and BTEX solubility data is provided. This review shows that historically, HC solubility has been largely ignored and basically unreported. Inlet sour gas compositions to the amine facility usually only include the concentration of H_2S and CO_2. The concentration of BTEX in the incoming sour gas is rarely reported. Even though these compounds are not reported it does not mean these compounds are not present. As many authors report, small concentrations of BTEX compounds have a devastating effect on the Claus process. Any absorption of BTEX by the amine sweetening solution could dramatically decrease the life of the Claus catalyst. Unfortunately, quantitative models to assess the absorption of BTEX in amine solutions have not been readily available, primarily due to lack of equilibrium data.

In 1972, Harbison and Dingman [21] described a Marathon plant that uses DGA to process casinghead gas. The sour gas composition is reported from methane to *n*-hexane along with the H_2S and CO_2 content. The composition and flow rates of HCs from the flash gas and the acid gas stream are provided. The authors make no mention of aromatic compounds.

In 1997 Skinner *et al*. [22] reported on the emission from regenerator vents for, methane, ethane, *n*-hexane and BTEX compounds. Data from six facilities, five DEA units and one MEA unit are reported. Process data including solvent circulation rates, HC content in the rich amine, and HC content in the rich flash are also provided. One interesting feature of this paper is that the BTEX emissions were measured using several different sampling methods including canister and rich amine.

Huval and Van de Venne [23] describe the Shedgum facility in Saudi Arabia.   Process operating conditions such as flow rate, temperature, pressure, circulation rates, and acid gas content are provided. The authors provide the amine plant inlet H_2S and CO_2 concentration and state that the inlet gas very rich with a molecular weight of 28. After amine sweetening, acid gas from the regenerator overhead contains about 17-35% H_2S.   This low concentration of H_2S in the acid gas requires a split flow Claus plant. Therefore, a significant amount of BTEX bypasses the Claus burner and feeds directly to the first Claus bed. Catalyst deactivation as a result of aromatic compounds prompted Harruff and Bushkuhl [24] to develop a novel process of using activated carbon to remove BTEX components in the acid gas stream. In 1998, Harruff [25] presents further results; the first published account of BTEX absorption in DGA from a gas treating facility. At that facility, the DGA solvent absorbs about 10 to 15% of the incoming BTEX components in the sour gas. The BTEX concentrations in the acid gas are about 200 to 250 ppm. The paper also describes an expansion process with a high-pressure field with greater H_2S content but also greater BTEX. If a common regenerator is used, this additional field would increase the BTEX in the acid gas to 450-700 ppm.

In 1997, Morrow [26] describes the patented BTEX-T.rex process to remove BTEX components from the rich amine prior to regeneration. A portion of the sweet gas is used as the stripping agent. The overhead of the BTEX-T.rex stripper could drive a direct-fired reboiler. For the case presented, the solution absorbs about 14 lb/hr of BTEX and the stripping tower removes about 70% of the BTEX from the solution. This case contains no H_2S.   For those cases with H_2S, a portion of lean amine may have to be fed to the top of the BTEX-T.rex stripping column to reabsorb H_2S.

In 1984, Law and Seidlitz [27] described the construction and the inlet gas composition for the Hanlon Robb facility. Initially, the facility was designed to use 30 wt% DEA. These authors report no BTEX compounds in the feed gas. Recently, Hagerty and Hawthore [10] describe the problems at the Hanlon Robb facility caused by

BTEX absorption in the amine plant even though there was not a dramatic change in the inlet feed. These authors report that the inlet gas contains about 1000 ppm BTEX. To produce an acid gas with higher H_2S concentration, the 30 wt% DEA solvent was switched to a 50 wt% MDEA solvent in 1995. This switch in solvents reduced amine circulation rates from 6165 to 3960 gpm. However, after the solvent switch, the catalyst in the first bed of the Claus plant deactivated in 6 months as a result of increased concentration of BTEX in the acid gas.

Claus Furnace BTEX Destruction and Catalyst Deactivation

Kohl and Nielsen [16] describe the Claus sulfur plant. Acid gas streams with H_2S concentrations from 50 to 100% use a straight through process. All of the acid gas is submitted to the Claus furnace. HC and BTEX compounds are destroyed provided a minimum temperature is achieved. Benzene is more difficult to destroy relative to other HCs. For acid gas streams with 20 to 50% H_2S, a straight through process is usually not possible since the acid gas stream does not have enough heating value to maintain a stable flame temperature. In this case a split flow process is used. A portion of the acid gas is bypassed around the reaction furnace. HCs and BTEX have a direct path to the Claus catalyst and deactivation is very likely to occur. Even low concentrations of BTEX may severely limit catalyst life.

Recent papers about burner design to destroy BTEX components have been published. Most of these modifications involve increasing the residence time in the burner and maintaining a sufficient temperature such that BTEX components are destroyed. Johnson *et al.* [28] describes different process options for a burner to prolong the catalyst life. These options included preheating the acid gas, acid gas enrichment, and oxygen enrichment. Klint [29] reports on data for the destruction of HCs in the Claus furnace. Straight chain HCs are relatively unstable and are nearly completely destroyed at the temperatures of the furnace. However, BTEX components are only destroyed when the temperature of the furnace is above 1050°C or 1922°F. Benzene is one of the more difficult compounds to destroy. Techniques to achieve a higher flame temperature such as oxygen enrichment, acid gas enrichment, preheating, and fuel gas spiking are discussed.

Until recently, most authorities agreed that to prevent catalyst deactivation, almost complete removal or destruction of the BTEX compounds is required. Even with BTEX concentrations in the 10 to 20 ppm range, catalyst deactivation is still a problem. Recently, Crevier *et al.* [30] showed that benzene is relatively benign to Claus catalyst deactivation. Toluene is slightly more harmful, and xylene is a catalyst poison. No data on the effect of ethylbenzene on catalyst deactivation is presented.

Because of the severe problems that BTEX absorption in amines can impart on sulfur recovery, other solvents such as *n*-formal morpholine are being investigated [30]. These solvents absorb more BTEX than amine solutions; however, the BTEX components are recovered in the overhead of the stripper with a three-phase separator.

HYDROCARBON SOLUBILITY MODEL DEVELOPMENT

The problem with quantifying and predicting BTEX absorption in amines is that very little data are available. Without data, no truly reliable models can be developed. In the absence of such data, engineers are forced to make assumptions such as using the properties of water as an initial estimate. As recent data show, this estimate is the minimum amount of BTEX absorbed. As more research and data become available, more robust models to quantity absorption of HCs in amine solutions will be developed. These models should provide better tools to engineers to account for BTEX and hydrocarbon absorption.

The technical development team at Bryan Research & Engineering, Inc. has developed a HC solubility model based on the previously mentioned HC solubility data along with other modeling strategies [10, 19]. This model is intended to represent the HC solubility in amine solutions as a function of temperature, pressure, and amine concentration and type. Using the limited data from Hagerty and Hawthorn [10] it appears that this approach can be extended to aromatic compounds. This model is currently available in the 98.2 version of TSWEET®.

Comparison of Model with Operating Data

To verify the model, comparisons with eight sets of plant data were devised. Simulations with TSWEET® were performed and the results are provided for the following cases. Other simulation programs with this capability

could also be used for this analysis. The facilities used to validate the model include a DGA, MEA, DEA, and MDEA. The DGA facility did not report any BTEX absorption.

Case 1. Yates DGA Facility

Table III reports the operating conditions of the Yates DGA facility as described by Harbison and Dingman [21]. Table IV compares the Flash Gas and Acid Gas HC concentrations relative to the reported values. The model tends to predict lower values relative to the reported values. There is fairly good agreement with all of the components except for *n*-C5.

Table III – Comparison Between Reported and Calculated
Process Conditions for the Yates Facility

			Simulation	
	Conditions	Reported	Setting	Calculated
Lean Amine				
	Temperature, °F	120	120	-
	DGA wt%	51.2	51.2	-
	Flow rate, gpm	172	172	-
	H_2S gr/gal	2	-	0.681
	CO_2 mol/mol	0.04	-	0.053
Rich Amine				
	H_2S mol/mol	0.09	-	0.084
	CO_2 mol/mol	0.18	-	0.153
Absorber				
	Trays	25 Real	8 Ideal	-
	Diameter, ft	-	3	-
	Weir Height, inch	-	3	-
	% Flood	-	-	40
Rich Flash				
	Pressure, psia	60	60	-
L/R Exchanger				
	Rich Outlet, °F	196	196	-
	Lean Outlet, °F	193	-	205
Regenerator				
	Trays	25 Real	12 Ideal	-
Condenser				
	Temperature, °F	100	100	-
	Reflux, gpm	10	-	9.5
	Pressure, psia	23	23	-
Reboiler				
	Temperature, °F	255	-	255
	Pressure, psia	27	27	-
	Steam Rate, lb/gal	-	1.3	-

Table IV – Comparison between Reported and Calculated Stream Compositions for

the Yates Facility

Component	Inlet	Sweet Gas		Flash Gas		Acid Gas	
		Reported	Calc.	Reported	Calc.	Reported	Calc.
	Mole%	Mole%	Mole%	Mole%	Mole%	Mole%	Mole%
H_2S	5.48	-	2.0e-6	1.40	0.798	48.19	45.37
CO_2	6.52	-	3.89e-3	0.37	0.093	51.12	53.96
N_2	0.16	0.17	0.182	-	0.065	0.02	7.76e-5
C1	74.0	83.01	83.97	78.93	82.43	0.46	0.370
C2	4.57	5.32	5.184	6.4	5.526	0.04	0.029
C3	3.46	4.14	3.925	5.08	4.103	0.04	0.020
i-C4	1.42	1.75	1.612	2.0	1.082	0.03	0.003
n-C4	2.10	2.63	2.382	2.6	2.630	0.04	0.016
i-C5	1.06	1.42	1.203	0.9	0.857	0.02	0.003
n-C5	0.24	0.31	0.273	0.65	0.200	0.02	6.5e-4
C6+	0.99	1.25	1.121	1.49	1.66	0.02	0.021
Conditions							
Temperature, °F	73	124	120	156	144	100	100
Pressure, psia	155	155	155	60	60	23	23
Flowrate, MMSCFD	6	-	5.28	4.7e-3	5.45e-3	-	0.724

Case 2. Regenerator Vent Emissions for DEA and MEA Facilities

Skinner *et al.* [21] provide the inlet compositions and operating conditions for these comparisons. The CO_2 composition for Case B and F were not reported and were assumed to be 3.5 and 6.3 mole%, respectively. Other modifications to the composition were necessary to ensure that the composition mole fractions summed to unity. No changes were made to the reported BTEX, methane, or *n*-hexane values. The solvent for Case B is MEA, and DEA is the solvent for the other cases. Table V compares the measured BTEX and hydrocarbon emissions from the regenerator vent with the calculated values. For Case A, the model tends to under predict ethane relative to the measured values. For Case B, the model tends to over predict *n*-hexane, benzene, and ethylbenzene. For Case C, the calculated values for ethane are low relative to the measured data while the calculated values for the BTEX components are high. For Cases D, E, and F the calculated values are in closer agreement. The model over predicts the absorption of xylene and under predicts the absorption of ethylbenzene. In most cases, the calculated values tend to agree with the Cannister Sampling Method. This method tends to show higher absorption relative to the other measurement techniques.

Table V - Comparison between Reported and Calculated Regenerator Vent
Emissions in Tons per Year

Components	Case A			Case B		Case C		
	Meas.		Calc.	Meas.	Calc.	Meas.		Calc.
	I[a]	II[b]		II		I	II	
Methane	22.1	NM[d]	22.416	NM	131.67	NM	NM	16.73
Ethane	5.8	NM	1.6455	NM	43.35	12.0	NM	1.913
n-Hexane	0.16	0.42	0.1228	0.096	0.4363	0.06	0.014	0.0247

Benzene	5.8	5.6	6.3601	5.5	12.04	7.5	7.1	10.07
Toluene	2.5	2.4	2.8073	2.5	2.735	3.5	3.2	5.0
Ethylbenzene	0.06	ND[e]	0.0952	0.019	0.146	0.06	0.08	0.1
Xylene	0.51	0.42	0.7031	0.41	0.2035	0.5	0.66	1.085

Table V - Comparison between Reported and Calculated Regenerator Vent
Emissions in Tons per Year (cont)

Components	Case D Meas.			Case D Calc.	Case E Meas.		Case E Calc.	Case F Meas.			Case F Calc.
	I	II	III[c]		I	III		I	II	III	
Methane	ND	NM	1057[g]	107.17	ND	312[g]	17.474	ND	NM	NR[f]	126.61
Ethane	8.68	NM		8.75	2.21		1.585	4.86	NM	NR	6.164
n-Hexane	ND	1.35	ND	0.6657	0.06	0.10	0.141	ND	1.1	0.12	0.209
Benzene	53.9	44.1	38.9	52.01	9.8	8.2	8.956	53.9	56.3	42.2	58.58
Toluene	29.3	23.7	22.4	29.86	5.7	5.3	5.475	47.0	45.7	34.8	47.13
Ethylbenzene	0.78	0.66	0.58	1.333	0.18	0.2	0.249	1.1	1.3	0.94	0.9558
Xylene	6.2	6.4	4.7	14.65	1.5	1.5	2.931	9.9	14.4	10.3	18.245

[a]Cannister Sampling Method.   [b] Amine Sampling Method.   [c] GC
Analysis Technique.
[d] Not Measured.   [e] Not Detected.   [f] Not
Recorded.
[g] Methane and Ethane Coeluted.

Case 3. Hanlon Robb DEA to MDEA conversion

Table VI provides the inlet composition and conditions for the Hanlon Robb calculations. The amount of BTEX in the feed was set at 1000 ppm and the distribution of the BTEX components was assumed to be similar to the Skinner *et al.* [22] facilities. Simulations with both the DEA and MDEA conditions were performed. Table VII shows that the 30 wt% DEA absorbed about 880 ppm BTEX; however, the switch to 50wt% MDEA results in BTEX concentrations of 1600 ppm. The reported methane value or 0.4 mole% in the acid gas is in agreement with the calculated DEA simulations or 0.31 mole%. However, the lower circulation of MDEA resulted in methane decreasing to 0.18 mole%. The reported BTEX concentration in the acid gas ranged from 750-1000 ppm and reached as high as 2500 ppm.

Table VI – Inlet Composition and Conditions
for the Hanlon Robb Simulations

Components	Mole%
Hydrogen	0.01
Nitrogen	0.576
Carbon Dioxide	9.692
Hydrogen Sulfide	9.514
Methane	78.27
Ethane	1.555
Propane	0.134
i-Butane	0.024
n-Butane	0.022
i-Pentane	0.01

n-Pentane	0.009
n-Hexane	0.02
n-Heptane	0.06
Octane	0.009
Benzene	0.0560
Toluene	0.0345
Ethylbenzene	0.0013
Xylene	0.0081

Conditions

Temperature, °F	85
Pressure, psia	1000
Flowrate, MMSCFD	300

Table VII – Comparison between Reported and Calculated
Acid Gas Composition for Hanlon Robb with Solvent
Switch from DEA to MDEA

Component	30 wt% DEA		50 wt% MDEA	
	Reported Mole%	Calc. Mole%	Reported[a] Mole%	Calc. Mole%
Hydrogen Sulfide	--	47.6	49.0	49.2
Carbon Dioxide	--	48.5	46.5	47.0
Methane	--	0.31	0.4	0.18
Aromatics	ppm	ppm	ppm	ppm
Benzene	--	578	--	942
Toluene	--	247	--	514
Ethylbenzene	--	5	--	15
Xylene	--	48	--	145
Total BTEX	--	878	750-1000 as high as 2500	1616

[a]Hagerty and Hawthorne [10].

Preliminary Calculations

Based on the eight comparisons with plant data using various solvents, it appears that the model can accurately predict hydrocarbon and BTEX absorption in amine solutions. Figure 2 shows the amount of benzene that would be absorbed per 100,000 lbs of solution for MEA, DEA, MDEA, and DGA. The figure is based on a single ideal stage at 100°F and 1000 psia. For all the amines, increasing amine concentration results in higher benzene absorption. Both MEA and DEA show less absorption than MDEA or DGA. If this figure was based on a molarity scale, the MEA and DEA would show nearly identical absorption and the DGA would show slightly greater pickup relative to MDEA. The other aromatic compounds show similar trends. Recent data actually shows DGA absorbs

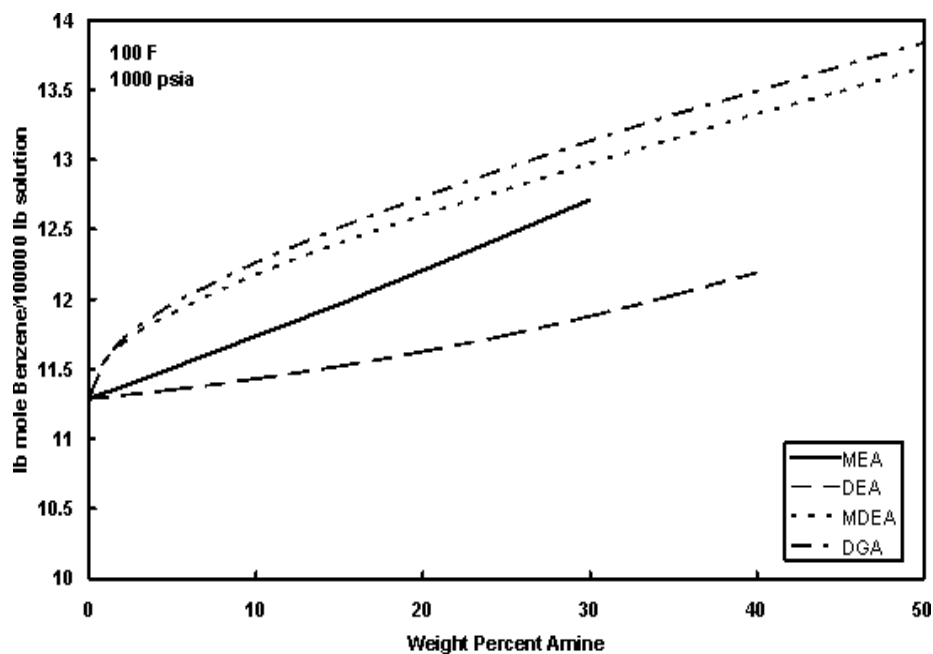slightly less benzene relative to MDEA [9].

Figure 2 - Calculated Benzene Absorption as a Function of Amine Type and Concentration

EFFECT OF PROCESS VARIABLES ON HYDROCARBON ABSORPTION

Amine type, concentration, and circulation rate are process variables capable of minimizing BTEX absorption. Other conditions such as the regenerator lean and semi-lean draws are simulated to verify that all light HCs are sufficiently removed. The effect of rich flash pressure and addition of makeup water is also investigated.

To minimize BTEX absorption in amines, MEA and DEA should be considered as opposed to the more concentrated solutions of DGA and MDEA. Furthermore, low amine concentration and low circulation rates also decrease HC and BTEX absorption. Steps to minimize BTEX absorption appear to conflict with the primary objective, economical acid gas absorption. Most amine units currently operating today were designed and optimized to meet the objective of acid gas removal to a required specification. Secondary effects such as HC and BTEX absorption were not emphasized. In the effort to process more gas with less utilities, amine units are shifting to more concentrated amine solutions. Many processes now use concentrated MDEA based solvents. As current research shows, this trend increases HC and BTEX absorption. Switching from MEA or DEA to high concentrations of MDEA could potentially double the BTEX absorption based on preliminary calculations. With concentrated solvents, BTEX and HC absorption can be decreased by increasing the rich acid gas loading [10]. This approach might also present problems, namely corrosion. Because the amine units are so tightly optimized with regard to solution strength and circulation rate to achieve a given acid gas specification, devising a similar amine process that will absorb less BTEX and HC compounds and maintains the current operating costs is nearly impossible. For example, by decreasing the solution strength to absorb less HCs, the process now needs a larger circulation rate which costs more to regenerate. Furthermore, the larger circulation rate incrementally absorbs additional HC and BTEX. However, if the total operating costs of the amine treating and sulfur recovery plant are combined together, an alternative process might readily present itself. Even though minimizing BTEX absorption is contrary to the primary objective of acid gas absorption, quantifying and predicting HC and BTEX absorption changes as a result of changes in solvent types, concentration and circulation rate is extremely useful in anticipating other process problems.

A typical amine regenerator operates at a low enough pressure and high enough temperature to remove light HCs and BTEX from the lean amine. Furthermore, if semi-lean amine is drawn from at least four real trays or two ideal

stages below the rich amine feed, the semi-lean stream should contain no appreciable amounts of HCs or BTEX.   If the draw is closer to the feed, residual amounts of HC and BTEX could appear in the semi-lean amine with the highest concentrations consisting of the heavier HCs.

For an amine unit with MEA or DEA, about 20-40% of the absorbed BTEX can be rejected in the rich flash [22, 31]. For an amine unit with high concentrations of MDEA or DGA, the rich flash can only reject about 5% of the absorbed BTEX [10]. In principle, the addition of makeup water to the rich amine should decrease the solubility of the HCs. In practice however, the addition of make-up water to the rich amine makes no significant change in the solution concentration.

If it is not possible to decrease HC and BTEX components to the regenerator overhead by one of the previously mentioned methods, other process modifications should be investigated. Two possible modifications that include physical separation are a hot flash with acid gas reabsorption and the BTEX-T.rex process. Figure 3 shows a hot flash process removing a portion of the BTEX compounds and than reabsorbing the acid gas components. Figure 4 shows a BTEX-T.rex process that uses a portion of the sweet gas as a stripping agent. The stripping gas removes some of the HC and BTEX compounds and a portion of the acid gas. Lean amine is fed to the top of the stripping column to reabsorb the acid gas components. Process simulation tools may be used to determine the maximum possible BTEX removal by these physical separation processes. If these processes are not capable of achieving the acceptable BTEX removal, the engineer may have to explore alternatives such as activated carbon.
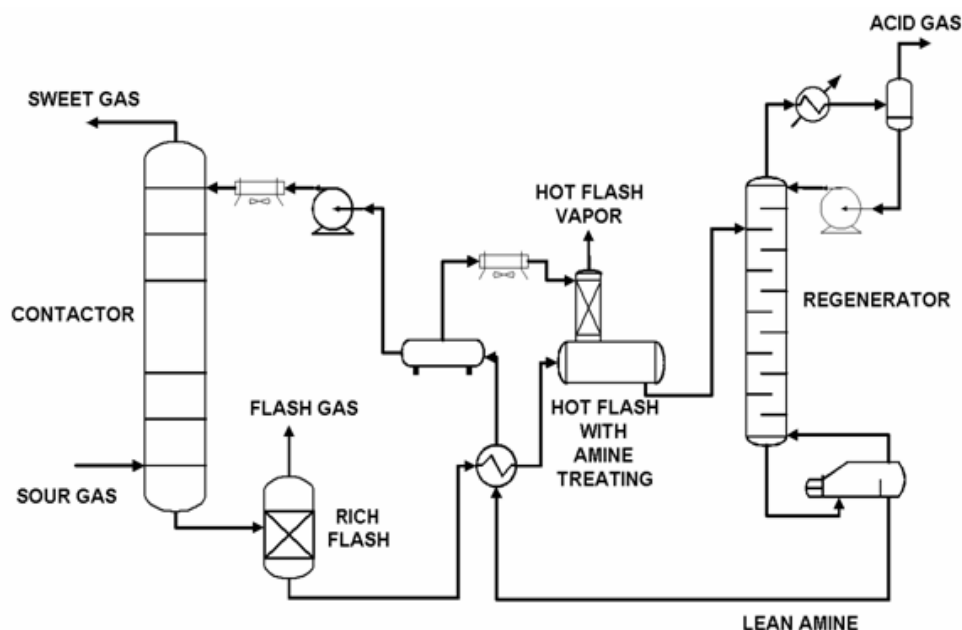

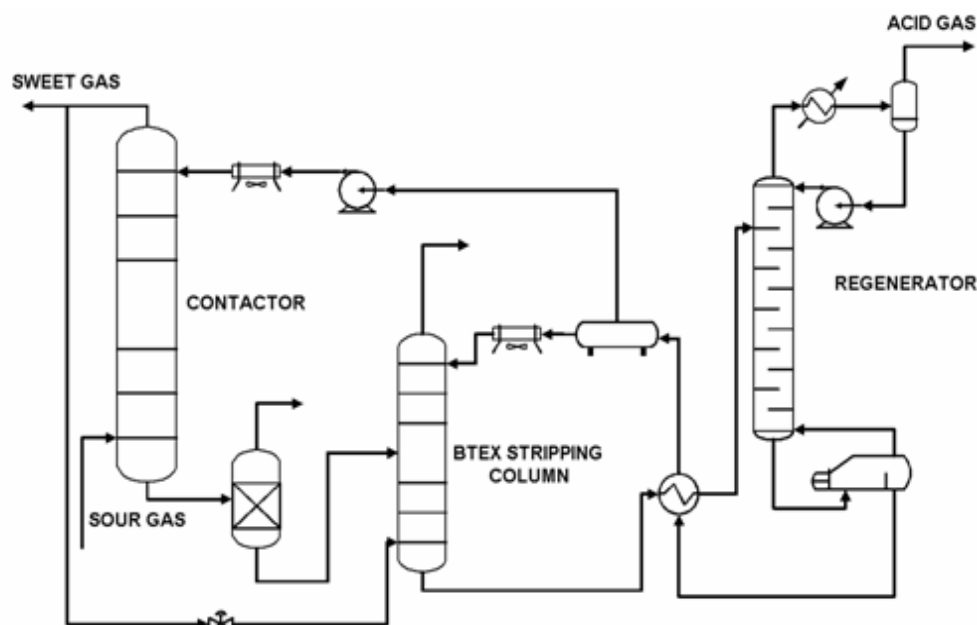Figure 3 - Amine Sweetening with Hot Flash

Figure 4- Amine Sweetening with BTEX-T.rex
Stripping Column

SHEDGUM FACILITY WITH HOT FLASH AND BTEX-T.rex STRIPPING COLUMN

This case is based on the data of Huval and van De Venne [23] and Harruff [25]. This is a 50 wt% DGA facility with a rich loading of 0.48 mol/mol. The lean amine temperature is 145°F. The rich amine at the bottom of the absorber is 180°F. A representative inlet composition to the amine facility was developed as shown in Table VIII. This composition yields a molecular weight of 28. The H_2S concentration from the regenerator overhead is 23% mole%. When 10% of the BTEX in the inlet gas is absorbed in the amine sweetening solvent, the resulting acid gas composition is approximately 250 ppm BTEX. Table IX compares the reported process conditions with the calculated values. This provides a model upon which to base the feasibility of using a hot flash or stripping process to remove BTEX components.

Table VIII – Inlet Composition and Conditions
for the Shedgum Simulations

Components	Mole%
Hydrogen Sulfide	2.9
Carbon Dioxide	7.9
Methane	56.0
Ethane	12.7
Propane	9.0
i-Butane	4.0
n-Butane	3.0
i-Pentane	2.0
n-Pentane	1.0
n-Hexane	0.5
Water	0.9913
Benzene	0.0150

Toluene	0.0100
Ethylbenzene	0.0008
Xylene	0.0053

Conditions

Temperature, °F	120
Pressure, psia	185
Flow Rate, MMSCFD	550
Molecular Weight	28

Table IX – Comparison between Reported and
Calculated Process Conditions for the Shedgum Facility

Process Condition	Reported	Calculated
H_2S Concentration in Acid Gas	17-35 Mole%	23.3 Mole%
Percent BTEX Absorbed	10-25%	12%
BTEX Concentration in Acid Gas	200-250 ppm	286 ppm

The hot flash pressure was decreased from 90 to 30 psia for temperatures of 180, 200, and 220°F. The lines on Figure 5 are calculated assuming that no lean amine is fed to the reabsorption tower. These lines represent the theoretical maximum removal of BTEX. With a temperature of 180°F, only 5% of the BTEX is removed. When the temperature is above 200°F and the pressure is below 60 psia, 50% removal of BTEX from the rich amine is possible. However, along with the BTEX removal, acid gas is also rejected to the vapor phase as shown in Figure 6. With 80% removal of BTEX, 28% of the acid gas has also been removed. This is most likely unacceptable.
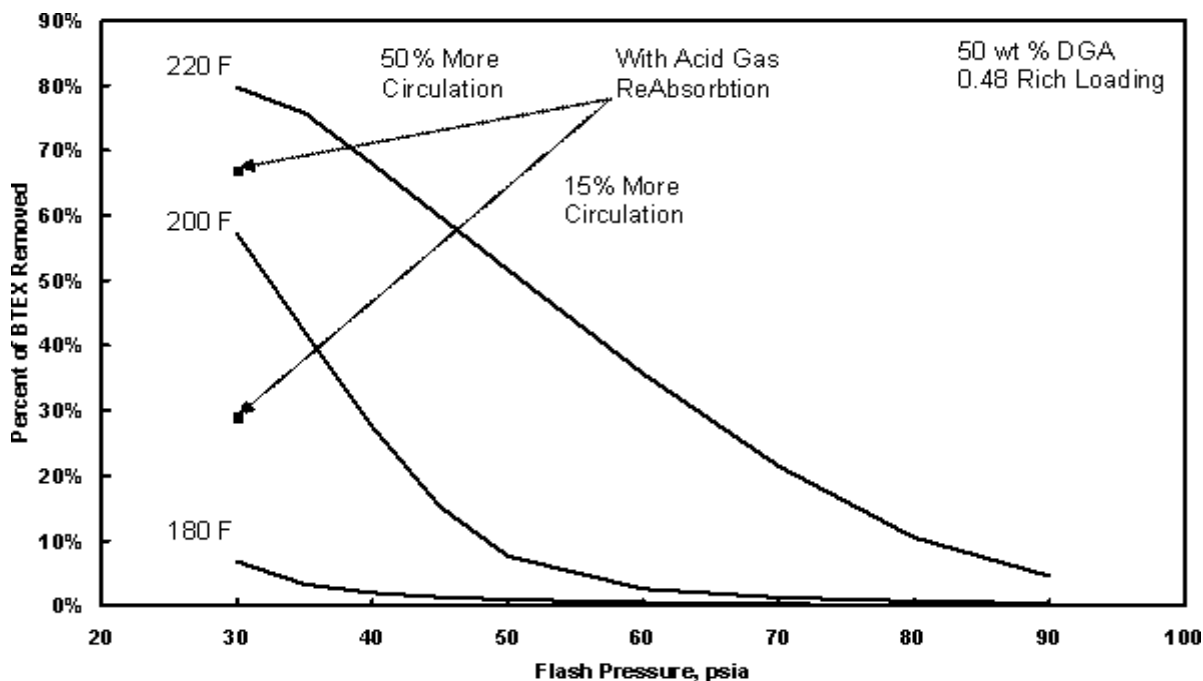
Figure 5 - The Effect of Hot Flash Pressure and Temperature on BTEX Removal
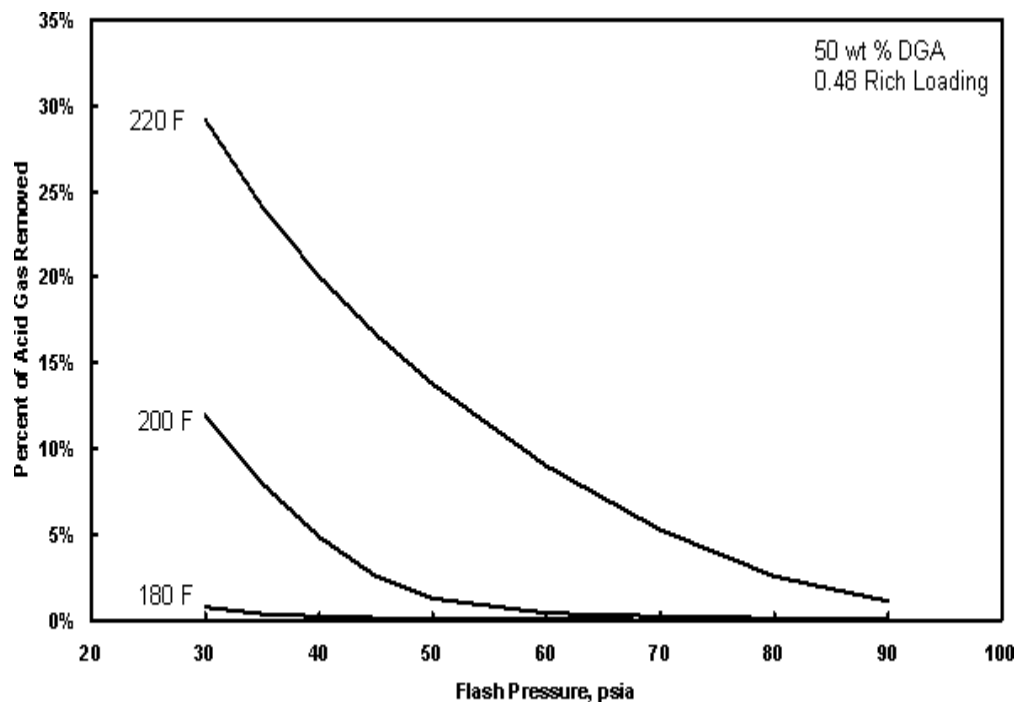

Figure 6 - The Effect of Hot Flash Pressure and Temperature on Acid Gas
Removal

To reabsorb acid gas, lean amine is fed to the top of the reabsorption column such that the overhead from the reabsorption column is 100 ppm H_2S. At 200°F and 30 psia, an additional 15% amine circulation rate is required. At 220°F and 30 psia, the additional amine circulation rate is 50%. The results of this reabsorption decreased the

BTEX removal from 80 to 68% at 220°F and from 55 to 30% at 200°F. The results of these calculations are shown on Figure 5. The temperature of the reabsorption column is extremely important. An adequate amount of lean amine must be fed to the column to decrease the temperature and absorb the acid gas. Too much amine may cool the column down to a level that the BTEX is also reabsorbed. If the circulation rate to the reabsorption column is increased, practically all of the BTEX removed in the hot flash is reabsorbed.

Simulations were also performed using the BTEX-T.rex stripping column with acid gas reabsorption. Figure 7 shows the results of these calculations. The percentage of sweet gas used as a stripping agent was varied from 1 to 5%. The lean amine circulation rate to the top of the BTEX-T.rex stripper column is set such that the overhead from the BTEX-T.rex column is 10 ppm H_2S. The long dashed line with the arrow pointing to the left in Figure 7 is the BTEX removal using the sweet gas. At a flow rate of 5% of the sweet gas, 60% of the BTEX is removed and the amine circulation rate is increased by 20%. The solid line represents a stripping gas containing no BTEX components. This is the theoretical maximum amount of BTEX removal for this process. The solid line shows that it is possible to remove 80% of the BTEX using a flow rate of stripping gas that is 5% of sweet gas and an amine circulation rate increase of 20%.
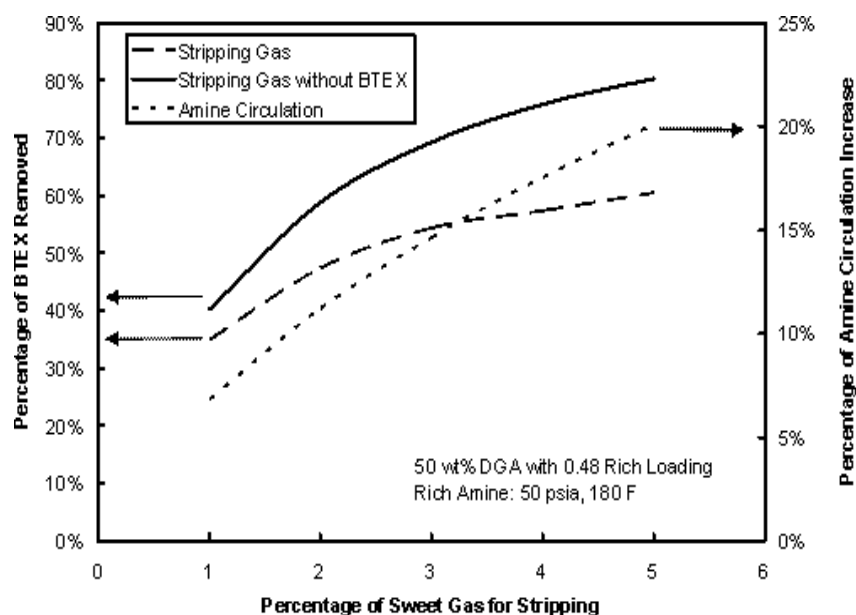

Figure 7 - BTEX Removal as a Function of Stripping Gas and Amine Circulation Rate

The magnitude of the BTEX removal for these processes is specific to this particular case study. However, regardless of the amine solvent or concentration, it is expected that similar trends will result. For other amine processes, engineers may use simulation tools to make similar evaluations. However, it appears a hot flash with reabsorption or the BTEX-T.rex stripping column with acid gas reabsorption cannot remove all of the BTEX from the amine solution. However, these processes may be used in conjunction with other techniques to minimize BTEX emissions and catalyst deactivation in the Claus plant.

RESULTS FROM PREVIOUS BTEX ABSORPTION MODEL

In 1998, Collie *et al.* [31] reports on total BTEX emissions from both glycol units and amine sweetening units. This report states that emissions from the investigated MEA, DEA and MDEA units would be 40 to 35 tons/yr. These values were based on a model that did not reflect the current available data. Using the current model, the emissions would be about 77 tons/yr for the MEA and DEA case and 322 tons/yr for the MDEA case.

At first glance, this appears to be an enormous difference, especially for the MDEA case. However, upon further

investigation, it appears that the comparison is not on the same basis. For the MEA and DEA cases the amine concentration was 20 and 30 wt%, respectively. This translates to a concentration of 3.3 and 3.0 on a molar basis, respectively. In contrast, the 50 wt% MDEA is 4.6 on a molar basis. The circulation rate is 600 gpm. The MEA and DEA cases have a rich loading of 0.5 mol/mol and sweet gas concentration of 40 ppm CO_2. For MDEA, the rich loading is only 0.287 mol/mol and the sweet gas is about 0.33 mole% CO_2. If the circulation rate of MDEA is decreased to 400 gpm and the amine is allowed to reach a rich loading 0.5 mol/mol, the overhead gas is 30 ppm CO_2. The calculated emissions for the MDEA case are 182 tons/yr. This is probably a more accurate comparison of the BTEX absorption for the various solvents since the objective of the sweetening unit and rich loading were maintained at similar conditions. However, it also shows the enormous impact that the type of amine and amine concentration has on calculated BTEX absorption. Other conclusions made by Collie *et al.* [32] are still valid: 25% of the emissions are attributable to the amine unit and 75% are due to the glycol unit, minimize circulation rate to decrease emissions and operate the amine absorber at lower temperatures to decrease total emissions.

Conclusions

Recent data on HC and BTEX solubility in amines have resulted in better quantitative models that have been incorporated into process simulation programs. These data show that the amine concentration and type is significant in affecting BTEX solubility. Increasing amine concentration and pressure increase HC and BTEX solubility while increasing temperature decreases HC and BTEX solubility (for typical commercial amine absorbers). Confirmation of the model with plant data for MEA, DEA, MDEA, and DGA suggests that the predictions may be used for engineering analysis and optimization. For amines such as TEA and DIPA, published operating data are yet to be made available.

With existing amine sweetening units, the quantity of BTEX absorbed in amine solvents affects down stream processes such as emissions, if the stripper is vented, or the sulfur recovery unit. BTEX components, especially xylene, severely limit Claus catalyst life. Techniques such as hot flash with acid gas reabsorption and stripping columns can remove a portion of the BTEX at the expense of additional amine circulation. Higher removal of BTEX may require additional processes such as absorption through activated carbon.

For the design of new sweetening units, engineers should not only include the primary objective such as acid gas removal but should also consider secondary effects such as HC and BTEX absorption. These secondary effects may dramatically change the Claus burner design temperature and residence time. More radical design modifications may have to be introduced. For highly integrated amine sweetening and sulfur recovery units, the optimum design includes amine concentration, circulation rate, burner design, and catalyst life.

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