BTEX Removal from Natural Gas Streams

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Executive Summary

BTEX (benzene, toluene, ethylbenzene, and xylene) is present in natural gas streams and is being picked up in amine and glycol dehydration units, being present in the exit CO2 and Water streams. As a result, incineration temperatures need to be increased and hence the cost of compliance with EPA emission limits (25 Tons/year) is large. Specifically, in the presence of BTEX the appropriate temperature is 1500 °F, whereas when other organics (like methane) are present one can incinerate at 1350 °F.

In order to cut down the cost of incineration, the removal of BTEX from various streams in the amine unit was researched. Different removal techniques such as minimizing absorption in the amine unit, removing in the amine unit, and removing prior to the amine treatment were researched. The best technique from an economic standpoint was the use of adsorbents in the acid gas stream. This was determined by comparing its cost with the savings produced by reducing the incineration temperature.

Adsorbents with the largest adsorption cost to extra incineration cost ratio were silica aerogels (SAG) and macroreticular resins (ionic resins). The aerogels were able to remove 8 ppmv of BTEX in a 575 MMSCFD stream of natural gas from the acid gas stream saving $100,000 when comparing the economics of removal with that of incineration. This was achieved by reducing the buying price of SAG from $37/kg to $34/kg at 14 cycles. Similar savings were found for ionic resins used in the acid gas stream by reducing the price of the resins from $43/kg to $35/kg. Both of these reductions could be achievable with long-term contracts with Cabot and Dow respectively. If the number of cycles is larger, then savings will further increase.

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Introduction

BTEX components are listed by the EPA in the Clean Air Act of 1990 as some of the 188 hazardous air pollutants. The EPA sets a standard of 25 tons per year for total aromatic compounds emitted in any given plant. There also exists 10 tons per year limit on each individual aromatic compound emitted. The reason for the restrictions are because benzene is a human carcinogen (promotes leukemia), toluene exposure can lead to reproduction or developmental effects, ethylbenzene affects the blood, kidneys, and liver and finally, xylene exposure can affect the central nervous system leading to respiratory and cardiovascular problems.

All gas companies must handle the emission of BTEX (benzene, ethylbenzene, toluene, and xylene) and C_{5+} which are absorbed in both the amine and dehydration units and released to the atmosphere if not incinerated properly. In order to reduce the emission of such compounds, one must incinerate these compounds at elevated temperatures.

This report evaluates more economical ways to remove BTEX other than incineration.

Background

We first briefly review how amine units work, then discuss the solubility of BTEX in amines and its estimation, the emission limits of BTEX, and the current cost of incinerating the BTEX emissions from amine unit. In the next section we discuss means of capturing the BTEX instead of incinerating it.

Amine Treating Units: Typical natural gas has the compositions of Table 1.

Table 1: Typical Composition of Natural Gas

Compound	Composition
Methane CH_4	70-90%
Ethane C_2H_6	0-20%
Propane C_3H_8	
Butane C_4H_{10}	
Carbon Dioxide CO_2	0-8%
Hydrogen Sulfide H_2S	0-5%
Nitrogen N_2	0-5%
Oxygen O_2	0-0.2%
Rare gases A, He, Ne, Xe	trace

In order to achieve pipeline “dry” gas quality from natural gas off the wellhead, the compounds must be separated from the methane. This is done by processing the gas through a series of processing plants that separate (when needed) the carbon dioxide and hydrogen sulfide, the water, the nitrogen, and finally, natural gas liquids (C2+). Carbon dioxide is removed from natural gas to increase the BTU value of the gas as well as to avoid the formation of carbonic acid, which will corrode pipelines while transporting the natural gas. The standard value for carbon dioxide in treated gas is 2% by volume, unless it is transported in LNG form, in which case the value is a lot lower. In turn, hydrogen sulfide is removed to prevent corrosion in pipelines, and reduce health risks. We focus mostly on amine units and we touch briefly on glycol units where similar solutions can be implemented.

Amine treating plants are the most popular processes used to remove the carbon dioxide and hydrogen sulfide. The process of amine treating is shown in Figure 1:

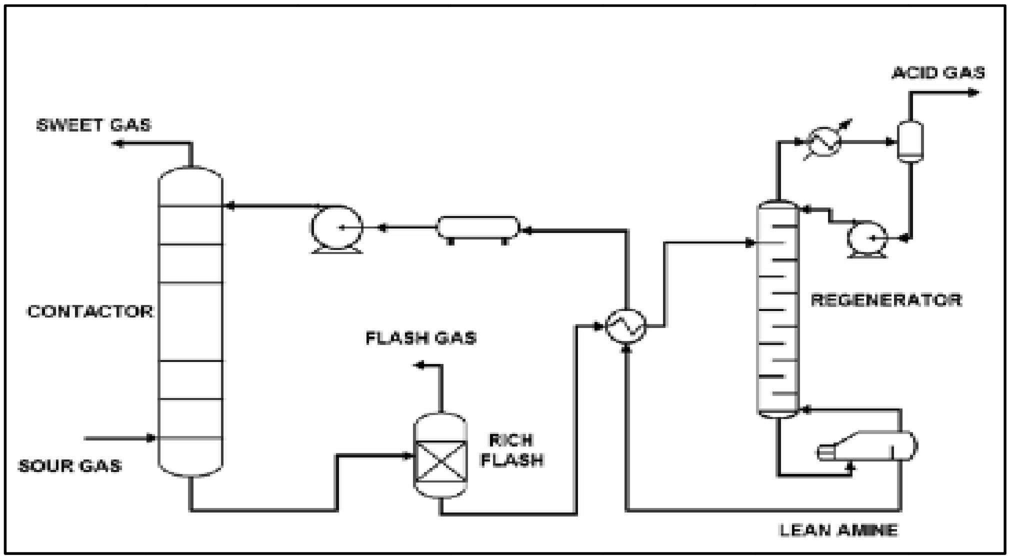
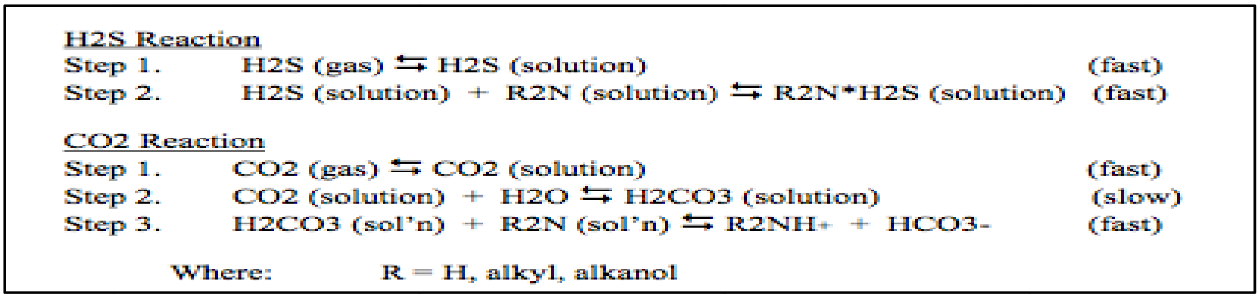


Figure 1: Amine Treating Unit (Bullin (2004))

Gas with CO2 and hydrogen sulfide contents above 5.7 mg per cubic foot of natural gas is called "sour gas". It enters the amine unit contactor where is exposed to a "lean" amine-water mixture, which is virtually CO2 and H2S free. This amine-water mixture absorbs majority of carbon dioxide and hydrogen sulfide. The natural gas leaves the contactor as "sweet gas", free of hydrogen sulfide and with low CO2 contents, while the "rich" (in CO2 and H2S) amine solution is sent to a regeneration unit.

The "rich" amine is first flashed at a lower pressure separate the vapor. The liquid mixture is then sent the regenerator where it is heated to high temperature to remove the contaminants. The liquid amine is then sent back to the contactor while the CO2 and H2S rich vapors are released from the regenerator as acid gas. This acid gas is then sent to an incinerator where it is burned to remove volatile organics and eventually harmful contaminants such as BTEX or it can be sent to a Claus unit to recover the sulfur.

The types of amines are used in industry are monoethanolamine (MEA), diethanolamine (DEA), di-isopropanolamine (DIPA), diglycolamine (DGA), and methyl diethanolamine (MDEA). These amines react with carbon dioxide and hydrogen sulfide as shown in Figure 2



<u>H2S Reaction</u>
Step 1. H2S (gas) ⇆ H2S (solution) (fast)
Step 2. H2S (solution) + R2N (solution) ⇆ R2N*H2S (solution) (fast)

<u>CO2 Reaction</u>
Step 1. CO2 (gas) ⇆ CO2 (solution) (fast)
Step 2. CO2 (solution) + H2O ⇆ H2CO3 (solution) (slow)
Step 3. H2CO3 (sol'n) + R2N (sol'n) ⇆ R2NH+ + HCO3- (fast)

Where: R = H, alkyl, alkanol

Figure 2: Amine Reactions (Shiveler, (2005))

On top of the above mentioned reactions, amines also participate in some side reactions with other components (CO, Sulfur compounds, Strong acids present in the gas) (Abdi) and lead to the degradation of amines. Thermal degradation happens as a result of high reboiler temperatures. Finally, reactions with carbon monoxide and sulfur can form formyl compounds

The reaction with strong acids, which enter through inlet stream (Abdi), cause heat stable salts to form. These salts can remain in the system and interrupt the absorption process. An amine reaction with strong acids is shown in Figure 3:

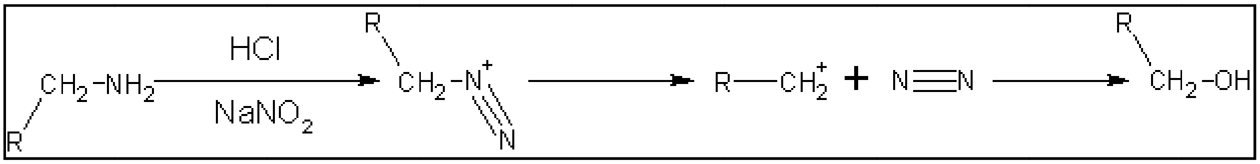


Figure 3: Reaction with strong acids

Incineration: Incineration involves the combustion of the acid gas and fuel. The oxidizer is shown in Figure 4. This gas is then contacted with a flame at the appropriate temperature to fully combust the gas. These oxidizers run at temperatures from 1000°F up to 1500°F for highly toxic VOCs. The "clean" exhaust gas contains mostly CO_2 and H_2O with some residual CO.

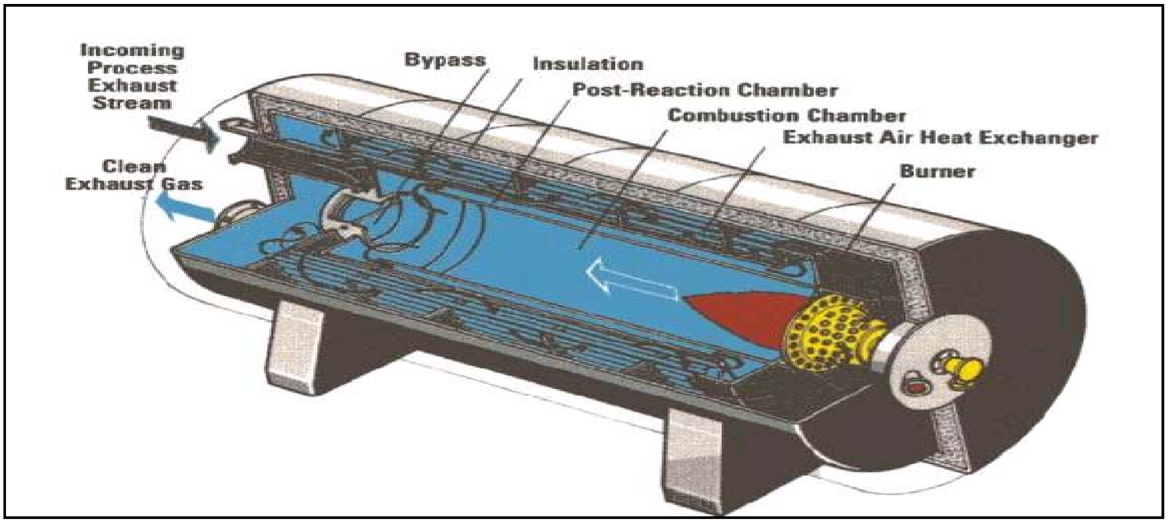


Figure 4: Example of Thermal Oxidizer *(Thermal Oxidizer Review)

Combustion is a sequence of exothermic reactions between fuel and oxygen, usually in the form of air. These reactions break down the fuel into carbon dioxide and water releasing mass amounts of heat. This same type of combustion happens in acid gas incineration in amine plants. The reactions that take place are the following:

$$\boxed{\begin{array}{l}
CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \\
C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \\
C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \\
C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O \\
C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O \\
C_6H_{14} + 9.5O_2 \rightarrow 6CO_2 + 7H_2O \\
C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O \\
C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \\
C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O \\
C_8H_{10} + 10.5O_2 \rightarrow 8CO_2 + 5H_2O
\end{array}}$$

Figure 5: Reactions in oxidizer

In order for VOC to combust, certain temperatures must be reached. These temperatures are given in Table 2:

Table 2: Auto ignition temperatures

Compound	AIT (°F)
Benzene	1097
Ethylbenzene	870
Toluene	997
Xylene	924
Methane	997
Ethane	859
Propane	842
Butane	788
I-Pentane	788
N-Hexane	437
N-Heptane	419

* (Lewandowski, 2000)

In order to combust at these auto ignition temperatures (AIT), long residences times must be used in the flame. In order to reduce this residence time to around .5 seconds for 99%

combustion, an additional 400°F is needed for about 99% combustion of VOCs. This combustion is done in thermal oxidizers. Thus, the temperature for incinerating BTEX needs to be near 1500°F. The temperature of incineration for acid gas when no BTEX is present is within the normal operating temperatures of the oxidizer since the ignition temperature for other compounds such as I-Pentane is 788°F. Therefore, this temperature is around 1350°F.

The EPA also monitors the amount of carbon monoxide and NOx admitted into the air by certain facilities. Carbon monoxide affects the respiratory system and in high levels can cause fatality. The EPA is trying to reduce these emissions but has set no real limits on it. NOx are monitored due to its affect of ground level ozone which can cause acid rain, affect global warning, and cause health problems such as respiratory issues. The overall goal of EPA is to reduce total NOx emissions to below 1.2 million tons in the US.

In order to restrict formation of these compounds, the amount of oxygen in the outlet of the oxidizer must be between 1-3%. The lower lime of 1% is set to reduce the amount of carbon monoxide that forms below this oxygen content. The upper limit of 3% is set to reduce the amount of NOx formed since these compounds are readily formed above this level of oxygen. Plant data from Williams' Ignacio plant are shown in Table 3:

Table 3: Ignacio Plant Data for Oxidizer

	Air	Fuel	Acid Gas
Flowrate (ft^3/hr)	355,888	23,162	504,042
Methane	0%	100%	0.50%
Carbon Dioxide	0%	0%	84.42%
Nitrogen	78.11%	0%	0%
Oxygen	20.95%	0%	0%
Argon	0.93%	0%	0%
Water	0%	0%	15.08%

This plant only incinerates the Acid Gas. The exit from the glycol unit is not burned but instead it is separated, and the BTEX is then sold. This data was validated with Pro-II and hand calculations to see if they are reproducible. Running Pro-II with the same inlets gave a temperature of 1421.21°F which is a 1.3% difference between the 1440°F reported in Ignacio data. The temperature calculated from this was 1430.72°F which has a 0.64% difference between real data and calculated data.

Ability of Simulators to Make Predictions in Amine Units

Commercially available simulators (AmineCalc, and Pro II) do not seem to predict the absorption of BTEX in the amine mixture well. On the other hand, the behavior of carbon dioxide in the amine unit is modeled more accurately only by Pro II, but not by Aminecalc. The main problem with BTEX in these simulators is the thermodynamics.

The interfaces AmineCalc, and Pro II are shown in figure 5 and 6 respectively.

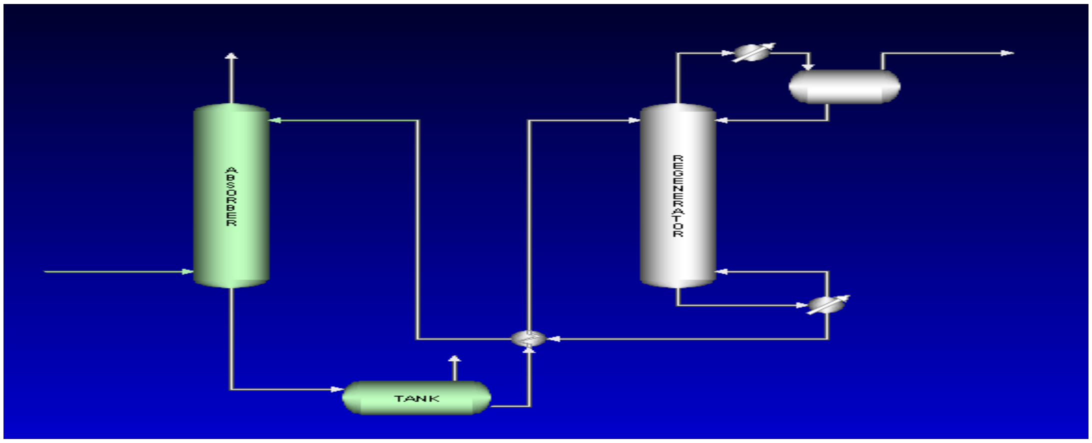


Figure 6. AmineCalc interface for Amine Unit.

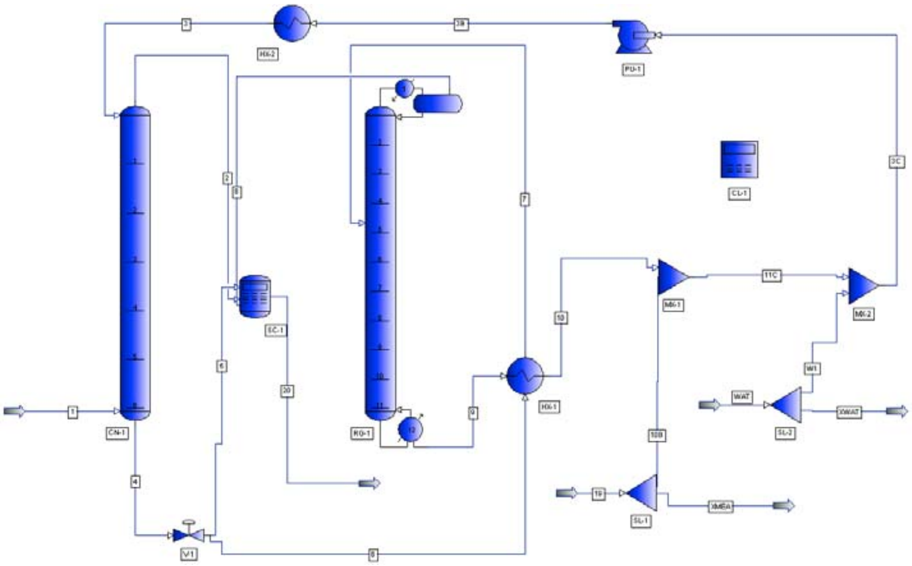


Figure 7: Screenshot of amine plant in Pro-II

AmineCalc and Pro II use the same set of chemical reactions to calculate the equilibrium constants. These are:

$$H_2O \overset{K_1}{\leftrightarrow} H^+ + OH^- \qquad (3)$$

$$H_2S \overset{K_2}{\leftrightarrow} H^+ + HS^- \tag{4}$$

$$HS^- \overset{K_3}{\leftrightarrow} H^+ + S_2^- \tag{5}$$

$$H_2O + CO_2 \overset{K_4}{\leftrightarrow} H^+ + HCO_3^- \tag{6}$$

$$HCO_3^- \overset{K_5}{\leftrightarrow} H^+ + CO_3^{-2} \tag{7}$$

$$RR'NH_2^+ \overset{K_6}{\leftrightarrow} H^+ + RR'NH \tag{8}$$

Both AmineCalc and Pro II use different equations of state (EOS). Aminecalc uses the Peng-Robinson EOS:

$$P = \frac{RT}{\left(\hat{V} - b\right)} - \frac{a}{\hat{V}\left(\hat{V} + b\right) + b\left(\hat{V} - b\right)} \tag{9}$$

Some of the problems with the EOS are the mixing rules used for the value of *a*. AmineCalc uses simple cubic mixing rules for calculating the values of a, which have been shown to be incapable of modeling real systems.

In turn, ProII uses the SRK EOS:

$$P = \frac{RT}{\left(\hat{V} - b\right)} - \frac{a\ \alpha}{\hat{V}\left(\hat{V} + b\right)} \tag{10}$$

This equation uses a different method for calculating the values of *a*, and these come from the study performed by Mathias-Klotz-Prausnitz. The equation used to calculate the value of *a* is:

$$a_{ij} = \left(a_i a_j\right)^{1/2} \left\{ \left(1 - k_{ij}\right) + \left(k_{ij} - k_{ji}\right) \left(\frac{x_i}{x_i + x_i} \right)^{c_{ij}} \right\} \tag{11}$$

This mixing rule has been shown to perform better than simple cubic mixing rules, but it is still not considered to be the best.

Finally Pro-II and AmineCalc recommend certain ranges for pressure, temperatures and amine concentrations (Tables 4 and 5). In addition Pro-II does not handle certain amines with high accuracy. Mixtures of amines are discouraged with this program. DIPA amine data is not good enough to scale up equipment around.

Table 4: Ranges of Pro-II for amine units

	MEA	DEA	DGA	DIPA	MDEA
Pressure, psig	25-500	100-1000			
Temperature, F	<275				
Concentration, wt% amine	15-25	25-35	55-65	50	30
Acid gas loading, g_{mole} gas/g_{mole} amine	0.5-0.6	0.45	0.5	0.4	

Table 5: Ranges of AMINECalc

	MEA	DEA	DGA	TEA	MDEA
Contactor Stages	22				
Temperature, F	77-260				
Concentration, wt% amine	0-30	0-50	50-75	0-50	0-50
Acid gas loading, g_{mole} gas/g_{mole} amine	< 1.0				

*(AMINE Calc User's Manual (1999))

Simulation Results: Data from a Williams's plant was used for the simulations. The inlet raw gas had a flow rate of 575 MM SCFD, 85 °F, and 500 psia. The amine flow rate was set at 702,176.88 gal/hr. The results from the simulations are shown in table 6, and this table will be used to compare the ability of the simulators to predict the ability of amines to pick-up carbon dioxide.

Field data from amine units from Williams has reported that the acid gas stream contains approximately 92 wt% of carbon dioxide. As seen in table 6, AmineCalc predicts that the acid gas stream contains 99 wt% of carbon dioxide, whereas Pro II predicts that the acid gas stream contains 94 wt% of the carbon dioxide. Thus, AmineCalc is over predicting the amount of carbon dioxide present in the acid gas stream. Also, as mandated by the EPA the sweet gas should contain less than 2 volume% of carbon dioxide present, and from table 6, it can be seen that the carbon dioxide present in the sweet gas stream is below the pipeline design guidelines.

Table 6. Results from AmineCalc and Pro II.

	Feed	***Sweet Gas***		***Acid Gas***	
Components (mol%)		*AmineCalc*	*Pro/II*	*AmineCalc*	*Pro/II*
CO2	9.37	3.12E-09	1.330	99.9500	87.050
Methane	89.57	9.83E+01	96.710	5.00E-02	0.392
Ethane	0.746	0.816	0.804	0.0004	8.521E-03
Propane	0.13	0.143	0.140	0.00006	1.364E-03
i-Butane	0.025	0.0275	2.698E-02	0	1.708E-04
n-Butane	0.025	0.0272	2.694E-02	0	4.588E-04
i-Pentane	0.046	0.0505	4.964E-02	0	3.659E-04
n-Pentane	0.005	0.0055	5.397E-03	0	3.537E-05
Hexane	0.009	0.00992	9.722E-03	7.11E-07	2.961E-05
Heptane	0.005	0.00552	5.403E-03	0	1.042E-05
Octane	0.01	0.011	1.081E-02	0	1.235E-05
Nonane	0.008	0.00884	8.650E-03	0.00E+00	2.308E-06
Benzene	0.0004	2.40E-05	4.020E-04	5.00E-05	2.850E-04
Toluene	0.0005	0.000311	5.219E-04	1.00E-05	1.655E-04
Ethylbenzene	0	0	0	0.00E+00	
Xylene	0.0002	9.14E-05	2.064E-04	0.00E+00	8.99E-05
N2	0.05	9.14E-05	5.384E-02	0.00E+00	1.04E-03
H2O	0	9.14E-05	0.814	0.00E+00	12.55
MDEA	0	9.14E-05	1.154E-04	0.00E+00	7.15E-17

We conclude that Pro II and actual BTEX show different liquid concentrations, but further experiments should be included in order to determine which simulator has a better prediction since no hard data is available. AmineCalc, on the other hand, is overestimating the amount of BTEX. Therefore, it can be concluded that AmineCalc and Pro II, or for that matter no simulator contains the right thermodynamics to deal with the presence of BTEX in the amine unit.

BTEX Solubility calculation in Contactor and Regenerator Tower: To obtain credible BTEX concentrations obtained experimental data is needed. Coquelet *et. al*. 2007, has calculated the values of the activity coefficients for BTEX, and these values will be used to calculate how much BTEX should be present in the contactor and regenerator tower.

Figure 8 shows the solubility of benzene, toluene, and ethylbenzene in DGA as a function of amine concentration and temperature. Figure 9 shows the activity coefficient of the benzene also as a function of amine concentration and temperature. By lowering this activity coefficient, the absorption onto the amine is raised causing more benzene or any other aromatic compound to be adsorbed more rapidly.

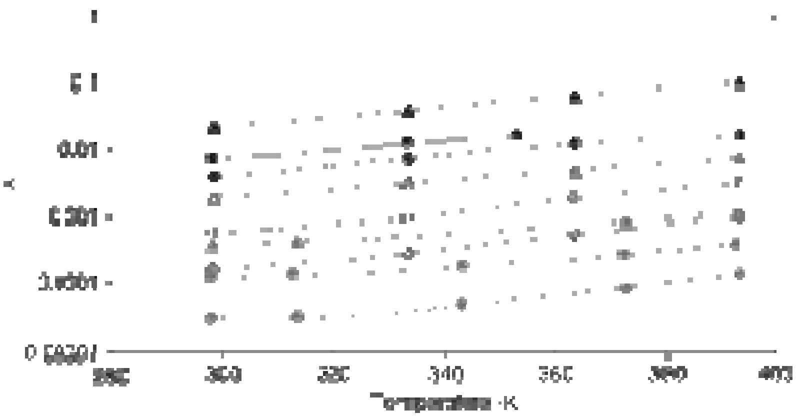


Figure 8: Solubility of Components of BTEX in DGA (Coquelet)

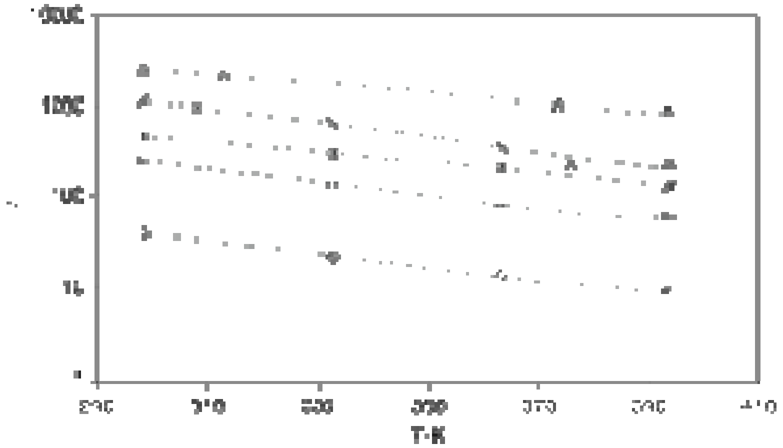


Figure 9: Effect of amine on activity coefficient of benzene.

Figure 10 and 11 shows the activity coefficients as a function of temperature for toluene and ethylbenzene respectively:

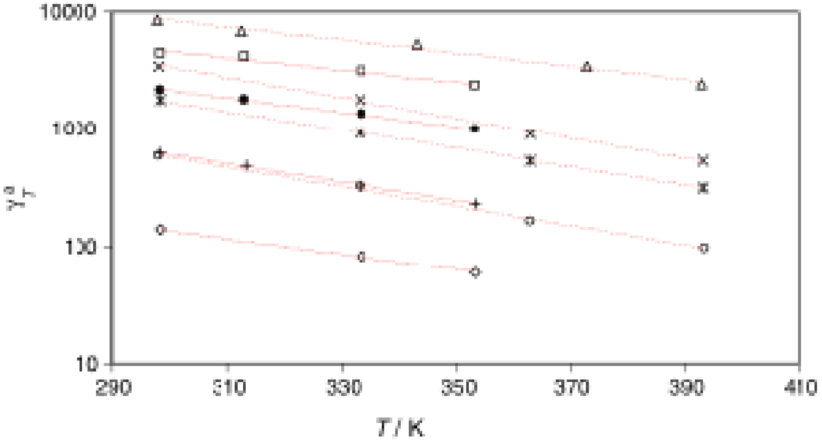


Figure 10. Activity coefficients as function of temperature for toluene.

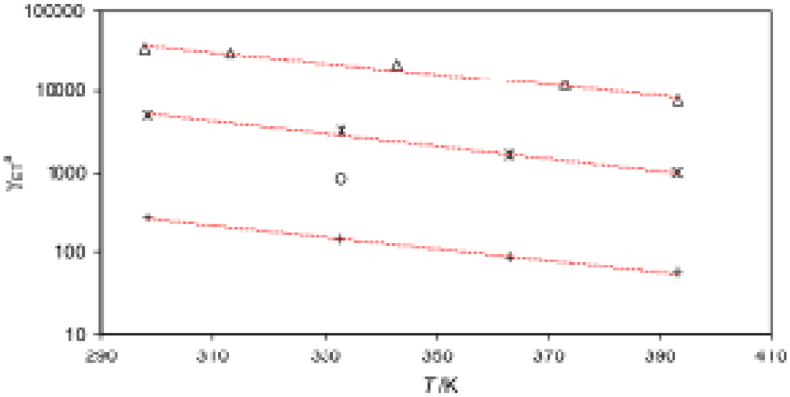


Figure 11. Activity coefficients as function of temperature for ethylbenzene.

In order to calculate the solubility of BTEX in the last tray of the contactor, the liquid and vapor streams coming out of trays 6 and 5 respectively were calculated. These flows were obtained from Pro II by using pseudo-streams (L_2 and V). Figure 12 shows how this was done in the simulator, and the pseudo stream are shown in the pink dotted lines. Data obtained from Pro II is reported in table 7. Now, the process taking place at the last tray is essentially a flash as shown in figure 12:

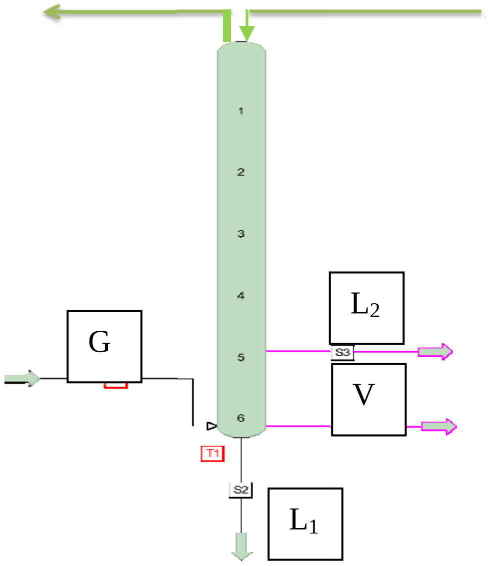


Figure 12. Contactor pseudo-streams from Simulator.

Table 7. Contactor pseudo-stream results from Pro II.

Contactor Data 575MMSCFD Feed and 702 MGal/hr MDEA				
Tray 5 T (F)	145			
Tray 5 P (psia)	250			
	G	*L2*	*V*	*L1*
Benzene (mol%)	4.00E-04	8.67E-06	4.00E-04	9.13E-06
Toluene (mol%)	5.00E-04	5.42E-06	5.02E-04	5.65E-06
Ebenzene (mol%)	0	0	0	0
Xylene (mol%)	2.00E-04	3.16E-06	2.02E-06	2.97E-06
Flow Rate (g-mol/hr)	2.86E+07	8.87E+07	2.85E+07	8.88E+07

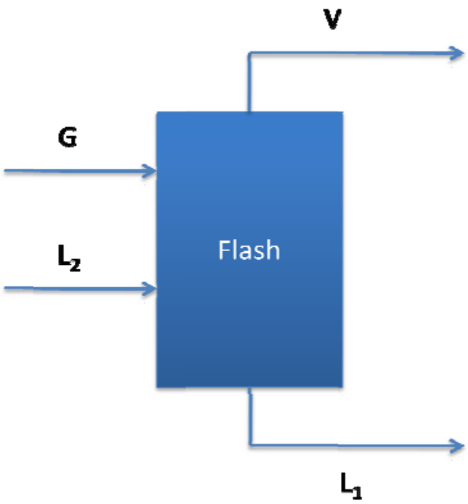


Figure 13. Last tray of contactor tower.

By doing a component balance, the following set of equations was obtained:

$$Gy_{BTEX}^{G} + L_2 x_{BTEX}^{L_1} = Vy_{BTEX} + L_1 x_{BTEX} \tag{12}$$

$$Py_{BTEX} = \gamma_{BTEX}(T) x_{BTEX} P^{sat} \tag{13}$$

$$Gy_{BTEX}^{G} + L_2 x_{BTEX}^{L_1} = V \frac{\gamma_{BTEX}(T) x_{BTEX} P^{sat}}{P} + L_1 X_{BTEX} \tag{14}$$

$$x_{BTEX} = \frac{Gy_{BTEX}^{G} + L_2 x_{BTEX}^{L_1}}{V \frac{\gamma_{BTEX}(T) P^{sat}}{P} + L_1} \tag{15}$$

$$x_{BTEX} = \frac{Gy_{BTEX}^{G} + L_2 x_{BTEX}^{L_1}}{V \frac{\gamma_{BTEX}(T) * 10^{6.89 - \frac{1203.53}{T + 219.89}}}{P} + L_1} \tag{16}$$

The last equation is used directly by taking the values of flows (*G*, *V*, L_1 and L_2) from Pro II. The reason why this is legitimate is because the BTEX concentrations are very low and their changes will not affect these flows. The flow of xBTEX is found and used to solve yBTEX.

In order to calculate the solubility of BTEX in the second tray, the liquid and vapor streams coming out of trays 2 and 3 respectively were calculated. Figure 13 shows how this was done in the simulator and the pseudo stream are shown in the pink dotted lines. Data obtained from Pro II is reported on table 8. The process taking place at the second tray is essentially a flash with the form indicated in Figure 14:

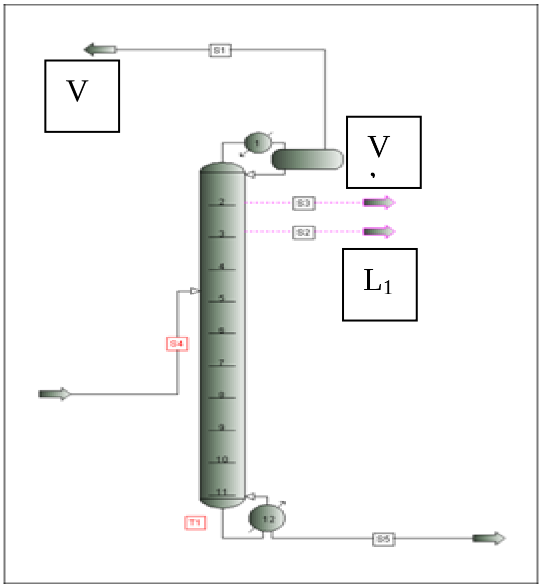


Figure 14. Regenerator pseudo-streams from simulator.

Table 8. Regenerator pseudo-stream results from Pro II.

Contactor Data 575MMSCFD Feed and 702 MGal/hr MDEA				
Tray 2 T (F)	211			
Tray 2 P (psia)	15.5			
	V'	*L1*	*V*	
Benzene (mol%)	2.01E-05	8.67E-06	2.85E-04	
Toluene (mol%)	1.17E-05	5.42E-06	1.66E-04	
Ebenzene (mol%)	0	0	0	
Xylene (mol%)	6.37E-06	3.16E-06	8.99E-05	
Flow Rate (g-mol/hr)	3.78E+07	8.87E+07	2.66E+06	

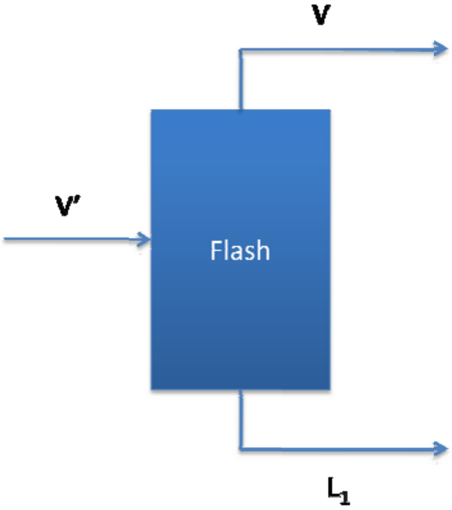


Figure 15. Second tray of regenerator tower.

By doing a component balance, as for the contactor tower, the following set of equations was obtained:

$$V' y^{V'}_{BTEX} = V y_{BTEX} \quad L_1 x_{BTEX} \tag{17}$$

$$P y_{BTEX} = \gamma_{BTEX}(T) x_{BTEX} P^{sat}$$

$$V' y^{V'}_{BTEX} = V \frac{\gamma_{BTEX}(T) x_{BTEX} P^{sat}}{P} + L_1 x_{BTEX} \tag{18}$$

$$x_{BTEX} = \frac{V' Y^{V'}_{BTEX}}{V \frac{\gamma_{BTEX}(T) P^{sat}}{P} + L_1} \tag{19}$$

$$x_{BTEX} = \frac{V' Y^{V'}_{BTEX}}{V \frac{\gamma_{BTEX}(T) * 10^{6.89 - \frac{1203.53}{T + 219.89}}}{P} + L_1} \tag{20}$$

In tables 9 and 10, the concentrations of BTEX obtained using our equations and experimentally obtained activity coefficients are compared with the results obtained from Pro II for the contactor and regenerator trays respectively. The same verification could not be done in AmineCalc because the flows in tray 5 from the contactor tower and tray 2 in the regenerator tower could not be obtained.

Table 9. Contactor Results.

BTEX Concentration from Experimental Results			
Component		***Contactor***	
		Calculated	*Pro II*
xi	Benzene	1.17E-06	8.67E-06
	Toluene	5.99E-07	5.42E-06
	EthylBenzene	0	0
	Xylene	2.78E-07	3.16E-06
yi	Benzene	2.46E-04	2.85E-04
	Toluene	1.46E-04	1.66E-04
	EthylBenzene	0	0
	Xylene	8.10E-05	8.99E-05

Table 10. Regenerator results.

BTEX Concentration from Experimental Results			
Component		***Regenerator***	
		Calculated	*Pro II*
xi	Benzene	4.79E-05	9.13E-06
	Toluene	9.96E-05	5.65E-06
	EthylBenzene	0	0
	Xylene	5.44E-05	2.97E-06
yi	Benzene	2.80E-04	4.00E-04
	Toluene	9.55E-04	5.02E-04
	EthylBenzene	0	0
	Xylene	2.35E-04	2.02E-06

It is our belief that Pro II produces good answers for flows and CO_2 concentrations in the amine unit. It is our suggestion to trust Pro II for the CO_2 concentrations. As far as the BTEX, we have proven that neither Pro II nor AmineCalc contains the right thermodynamics for the amine unit. From solubility data, we were able to reproduce the correct concentrations of BTEX in the contactor and regenerator towers. These values will have to be compared to data obtained from the plants.

Ability of Simulators to Make Predictions in Glycol Units

The Glycol units are designed to remove water present in the sweetened gas. A Glycol dehydration unit can be modeled in GlyCalc and Pro II, and the interfaces for these simulators are shown in figure 16 and 17 respectively.

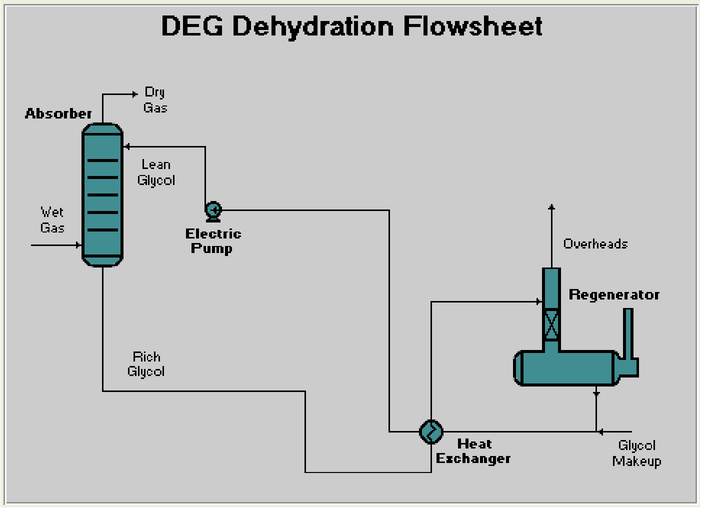


Figure 16. Glycol Dehydration Unit interface for GlyCalc.

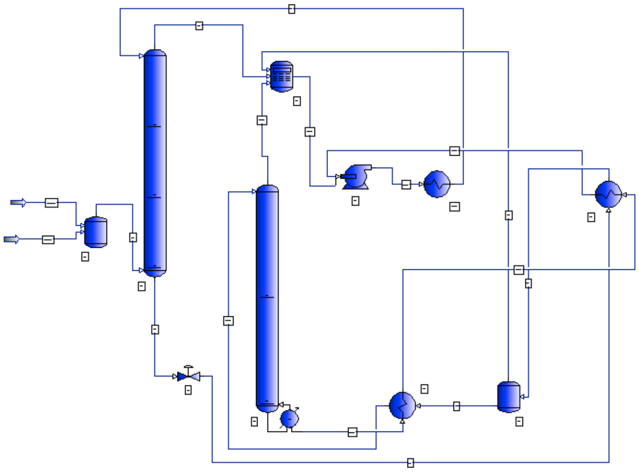


Figure 17. Glycol Dehydration Unit interface for Pro II.

Pro II uses a special thermodynamics package called GLYCOL which uses SRK EOS, with the modification from Mathias-Klotz-Prausnitz added to calculate the binary interaction coefficients; (this is the same EOS used in the amine package). One of the limitations with this thermodynamic package is that some of the binary interaction coefficients for some species are not present, even though some of these components might not be present in significant quantities.

The manual recommends a temperature range from 80-400 °F, and a pressure limit of 2000 psia. It also uses rigorous tray by tray calculations with appropriate enthalpy calculations.

.

Glycalc, in turn, makes some modeling assumptions: Around the absorber, the water mass balance can be calculated in two ways: either the number of theoretical stages is given or the amount of dry gas can be specified. If the number of stages is given, the program uses the Kremser-Brown approximation for the absorption of each compound. This approximation is done by using the following equation:

$$\frac{Y_{n-1}-Y_1}{Y_{n-1}-Y_o}=\frac{A^{n-1}-A}{A^{n-1}-1} \qquad (21)$$

where A is the average absorption factor, Y_{n-1} is the mole fraction of compound in wet gas entering absorber, Y_1 is the mole fraction of compound in dry gas exiting absorber, Y_o is the mole fraction of compound in the vapor phase that is in equilibrium with lean glycol, and n is the number of theoretical stages. In turn, the average absorption factor A is given by:

$$A=\frac{L}{KV} \qquad (22)$$

where L is the average liquid glycol flow rate and V is the average gas flow rate in column. Thus, the contactor tower is not modeled rigorously by using a stage by stage flash calculations, average values of K are used. .

For the regenerator, the manual notes that "*to avoid complex heat and material balances that would be needed if the regenerator were rigorously modeled, a simple empirical calculation is used*".

Furthermore, the manual adds that "*the use of stripping gas can also reduce the amount of organics remaining in the lean glycol, however, for the sake of simplicity, GlyCalc does not attempt to determine the impact of stripping gas on the removal of organics from the rich glycol*".

Therefore, the program assumes that the fraction of each component that is removed from the glycol in the regenerator is assumed to be the same, regardless of whether stripping gas is used or not.

Simulator Results: Data obtained from the Williams's Milagro plant was used for the simulations. The inlet gas had a flow rate of 49 MM SCFD, 104 °F, and 887 psig. The glycol circulation rate was set at 10 gal/min, at a temperature of 382°F. The results from the simulations are shown in table 11.

Pro II and GlyCalc produce good answers for flows and close results for H_2O concentrations in the glycol unit. Since no real data is available at this moment, no comparison can be drawn at this moment as to what simulator more accurately predicts the concentrations of H_2O. GlyCalc produces better results for BTEX concentrations in glycol dehydration unit in comparison to data in table 11.

As far as the regenerator results, one would be able to accurately predict how much BTEX is present, since GlyCalc can reproduce the results of the contactor tower. What GlyCalc would not be able to predict is the amount of duty needed in the regenerator since the simulator does not solve the energy balance, but instead uses a simple correlation.

Table 11. Results from GlyCalc and Pro II without BTEX.

	Feed	Dry Gas		
Components (mol%)		GlyCalc	Pro II	Milagro Data
Methane	98.8880	98.9	98.880	98.9160
Ethane	0.8164	0.816	0.816	0.7994
Propane	0.1605	0.16	0.160	0.1556
Isobutane	0.0263	2.630E-02	2.619E-02	2.51E-02
n-Butane	0.0262	2.620E-02	2.603E-02	2.53E-02
Neopentane	0.0003	N/A	5.213E-03	3.00E-03
Isopentane	0.0086	N/A	8.581E-03	8.30E-03
n-Pentane	0.0053	5.290E-03	5.286E-03	5.10E-03
2,2-Dimethylbutane	0.0003	N/A	2.838E-04	3.00E-04
2,3-Dimethylbutane	0.0006	N/A	5.524E-04	6.00E-04
2-Methylpentane	0.0017	N/A	1.571E-03	1.60E-03
3-Methylpentane	0.0009	N/A	8.094E-04	9.00E-04
n-Hexane	0.0016	1.600E-03	1.584E-03	1.50E-03
Heptanes	0.0051	5.070E-03	5.029E-03	5.20E-03
Octanes	0.0003	5.920E-03	2.895E-03	5.00E-03
Nonanes	0.0006	N/A	5.582E-04	3.00E-04
Decanes plus	0.0004	N/A	3.524E-04	1.10E-03
Nitrogen	0.0569	5.690E-02	5.687E-02	5.29E-02
Carbon Dioxide	0.0000	0	0	0
Oxygen	0.0000	0	0	0
Water	N/A	4.860E-03	5.804E-03	N/A
Benzene	3.000E-04	2.720E-04	2.189E-04	3.000E-04
Toluene	5.000E-04	4.220E-04	3.281E-04	4.000E-04
Ethylbenzene	0	0	0	0
Xylene	6.000E-04	3.930E-04	2.459E-04	3.00E-04
2,2,4-Trimethylpentane	1.000E-04	9.980E-05	9.912E-05	1.00E-04
Cyclopentane	0	0	0	0
Cyclohexane	9.000E-04	8.880E-04	8.744E-04	9.00E-04
Methylcyclohexane	1.000E-03	9.840E-04	9.851E-04	1.10E-03

BTEX Removal Solutions

Another way to approach the issue of BTEX removal from amine plant is to restrict of eliminates the issue from happening. This can be done by three different possibilities:

- Run the amine unit at parameters which are ideal to decrease BTEX absorption.
- Run the amine unit to maximize BTEX absorption and remove within the process To avoid incineration
- Remove BTEX from the natural gas stream prior to entry into treating unit.

All three of these are investigated and discussed below in detail. But first the economics of incineration is discussed.

Incineration Economics: We use Williams' Milagro plant that processes 575 MMSCFD of gas containing 8 ppm BTEX. We compute the savings from the reduction of temperature from 1500°F to 1350°F. Using the knowledge of a 2% goal for oxygen in what is released to atmosphere, the amount of methane and cost on a $5/MMBtu basis was calculated for 1500°F and 1350°F. This reduction can be done due to the lower AIT for the trace hydrocarbons in the acid gas stream. Table 12 shows these amounts:

Table 12: Reduction of Temperature Results

Thermal Oxidizers Analysis		
With BTEX		
Amount of CH4 (MMft^3/year)	Cost per year	Cost per Day
221	$1,117,000	$3,000
Without BTEX (Constant Air Excess Assumed)		
Amount of CH4 (MMft^3/year)	Cost per year	Cost per day
161	$814,000	$2,000
Saving per Year ($)		
$303,000		

We now discuss removal solutions and compare with this cost.

Adjusting Amine Treating Parameters: In order to reduce the absorption of BTEX into amine, a few of the parameters of the treating process can be looked at and modified. These parameters consist of temperature of rich amine, pressure of contactor column, circulation rate type of amine, and concentration of amine. These parameters were tested and researched in Bullin (2004). They are shown in Figures 18 and 19. In order to compare effect of temperature, Pro-II simulations were run to back up Bullin's discoveries (Figure 18). Bullin concludes that the higher the "rich" amine temperature, the lower absorption until a CO_2 cutoff is reached where anything above this temperature does not adsorb enough CO_2. In addition, running at higher temperature causes the reboiler and heat exchangers to have higher heat duties. The pressure dictates the partial pressure of BTEX, but it is more affected by inlet conditions and amine conditions so it is hard to control directly.

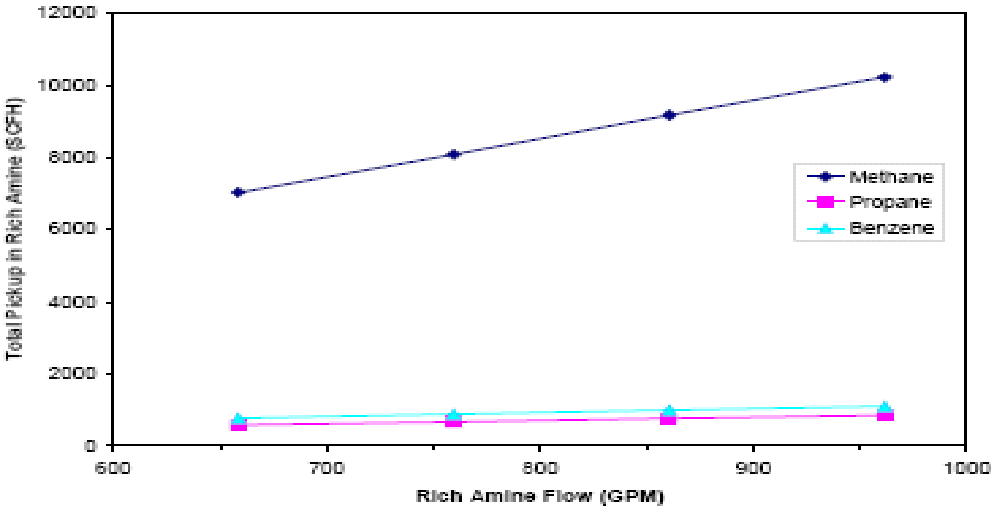


Figure 18: Absorption of Benzene compared to circulation rate (Bullin 2004)

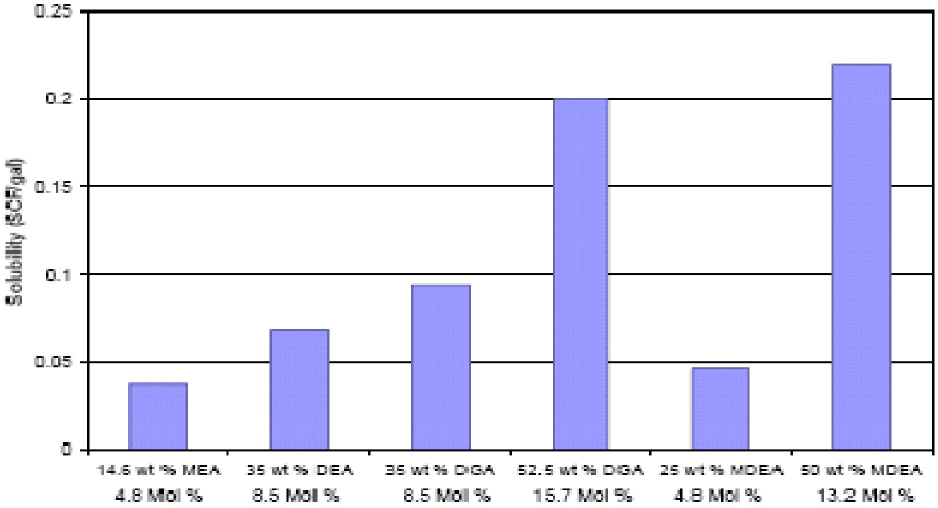


Figure 19: Absorption of toluene amine type and concentration (Bullin 2004)

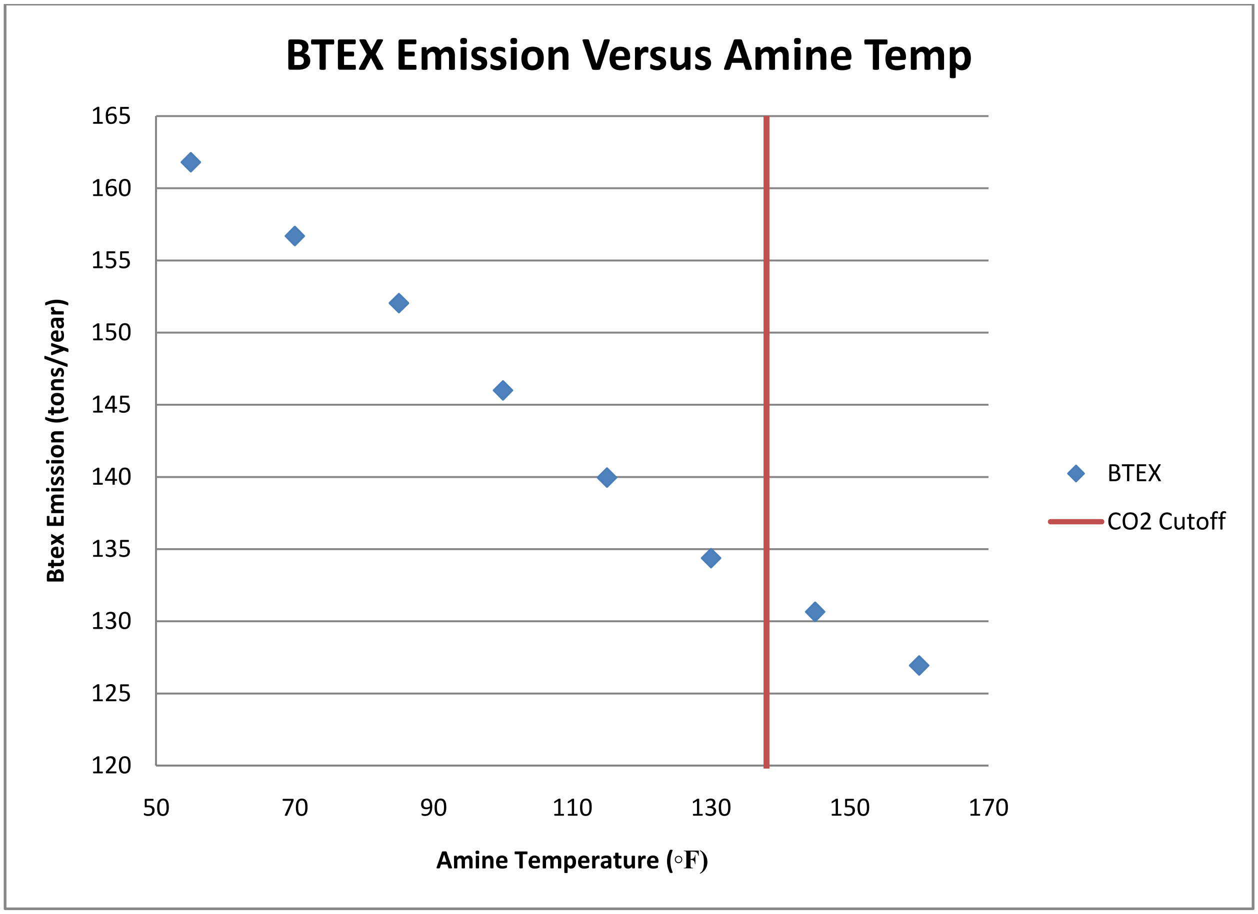


Figure 20: Temperature trials for benzene absorption

Regarding amine circulation, the higher the rate then the more BTEX is absorbed. This circulation is already reduced to lowest possible to prevent excessive corrosion in the system. The lower the concentration of amine, the less BTEX it picks up. In addition, the higher the amine in terms of tertiary, secondary, or primary, then the higher the concentration can be used to achieve same absorption rate. This does not solve the problem due to high temperatures of amines are needed in order to reduce the BTEX emissions below the 25 tons per year limit. This high amine temperature will exceed the carbon dioxide cutoff of 2% required in outlet gas.

Use of Water: In order to remove benzene from the feed gas, one can take advantage of the solubility of benzene in water. The process flow diagram is shown in figure 21.

Tsonopoulos (1983) found an empirical correlation for Henry's constant as a function of temperature. This expression is shown below:

$$\ln H = A + \frac{B}{T} + CT^2 + D\ln T \qquad (23)$$

where A, B, C, and D are constant shown in table 18.

Table 13: Constants for Henry's equation for Benzene

Empirical Constants for Henry's Constant as a Function of Temperature				
Benzene	***A***	***B***	***C***	***D***
	132.977	-9463.470	-1.506	-16.927

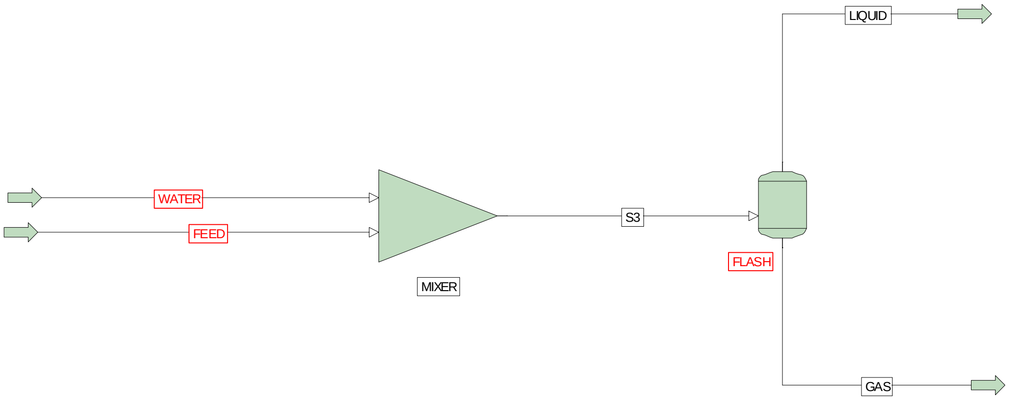


Figure 21. Process flow diagram for addition of water

Now, we proceed with the mass balance. We have:

$$F_{H_2O}x_B + F_F y_B = F_L x_B^{'} + F_G y_B^{'} \tag{24}$$

where F_{H2O} is flow of water into mixer, x_B is concentration of benzene in water, F_F is flow of feed gas, $y_{\mathbf{B}}$ is the concentration of benzene in feed gas, F_L is the flow of liquid out of mixer, x'_B is the concentration of benzene in the stream out of the mixer, F_G is the flow of the gas out of the mixer, and y'_B is the concentration of benzene in gas out of mixer.

The composition of benzene in the feed is usually around 0.4-100 ppm. Therefore, if we simplify our example and say that most of the BTEX is benzene, we have our composition in the feed stream. The composition in the water feed stream depends on how the liquid stream coming out of the flash drum is dealt with. If the benzene is removed from the water, and then the water is recycled, some benzene will be present when mixed with the feed gas. If the liquid stream containing the benzene is incinerated, then the water mixed with the feed gas will contain no benzene. Finally, the composition of benzene in the liquid stream will depend on the Henry's constant of benzene in water. The equation relating the concentration of benzene in water is shown below:

$$x_{B,w} = \frac{P_B}{H_{B,w}} \tag{25}$$

where P_B is the partial pressure of benzene. Now, we proceed to present how the problem would be solved if there was no recycle stream present.

If there is no BTEX in the recycled water, then the concentration of benzene in the water will be zero, so we will get:

$$F_F y_B = F_L x_B^{'} + F_G y_B^{'} \tag{26}$$

and equation 26 can be further simplified to:

$$y_B^{'} = \frac{F_F y_B - F_L x_B^{'}}{F_G} \tag{27}$$

equation 16 will tell us how the concentration of benzene in the gas changes as the flow of water is increased or decreased. Trials were run on a inlet gas stream with the following composition:

Table 14: Composition of gas

Methane	83%
Ethane	6%
Propane	4%
Butane	2%
Heptane	0.55%
Hexane	0.42%
CO2	4%
Benzene	0.03%
Total	100%

To obtain results, we used gas was flowing at 100 MMSCFD at 25°C and 200 psia. Using the method described earlier and solving for amount of benzene in the outlet gas stream assuming complete separation of benzene of water or no recycle used is represented below:

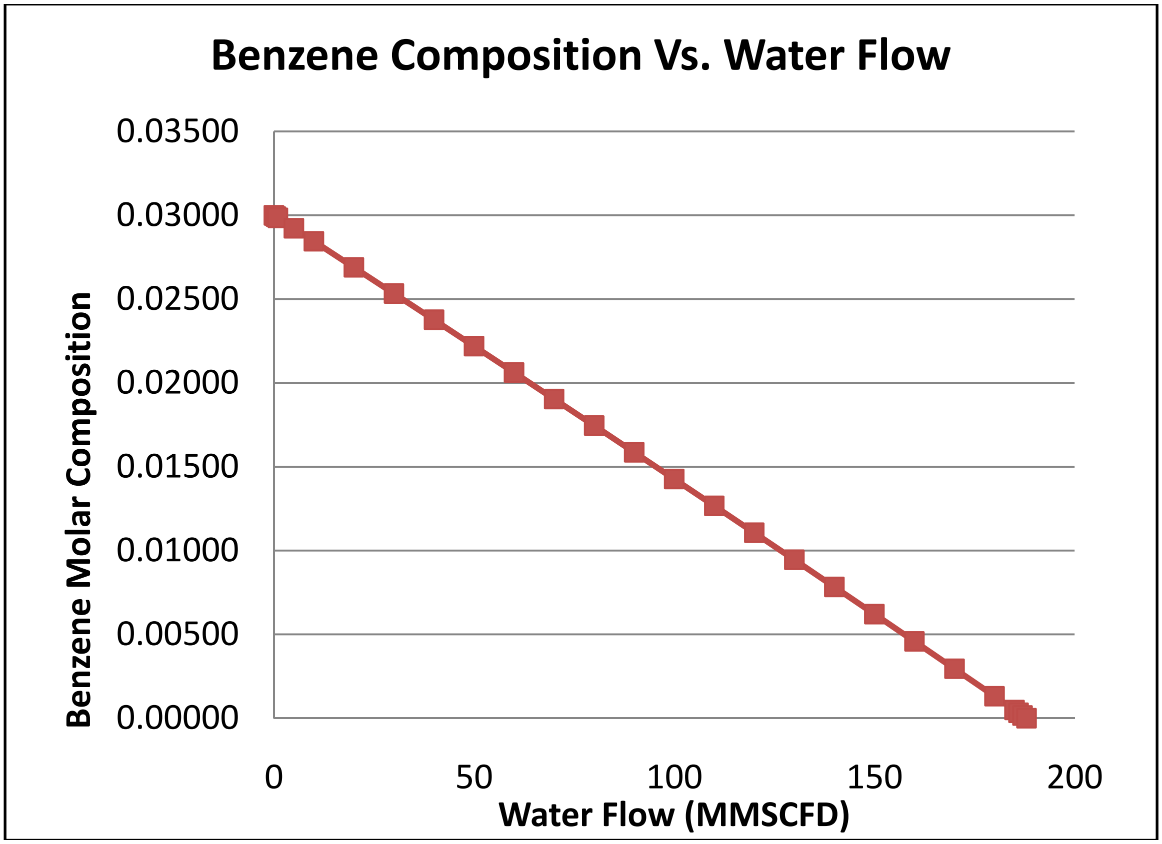


Figure 22: Composition of Benzene with Water Flow

The above figure shows how for a flow rate of 100MMSCFD of natural gas, about double the water flow is required to reduce the amount of benzene in the gas from .03 mole percent to negligible amounts. On top of that, the water would have to then be treated to remove benzene. This would require some sort of adsorbent such as a surfactant modified zeolites as in Ranck (2005). This would be an additional cost on top of the solvent.

This was also solved assuming best case scenario of nothing else absorbing into the water besides benzene. This would not be true for methane does absorbs in water although not as readily as benzene since Henry constant of methane is about 100 times the Henry constant of benzene (http://www.handpmg.com/lustline29-oh-henry.htm). This trial proves that the use of water as a solvent is not a viable option. In addition, most solvents would require the removal of BTEX in order to reuse or dispose of the solvent.

Use of Activated Carbon: Activated carbon (AC) is an adsorbent used in many industries such as water filtration and vent gas emissions. Many companies produce activated carbon making it readily available for purchase at low cost. Activated carbon has the following properties:

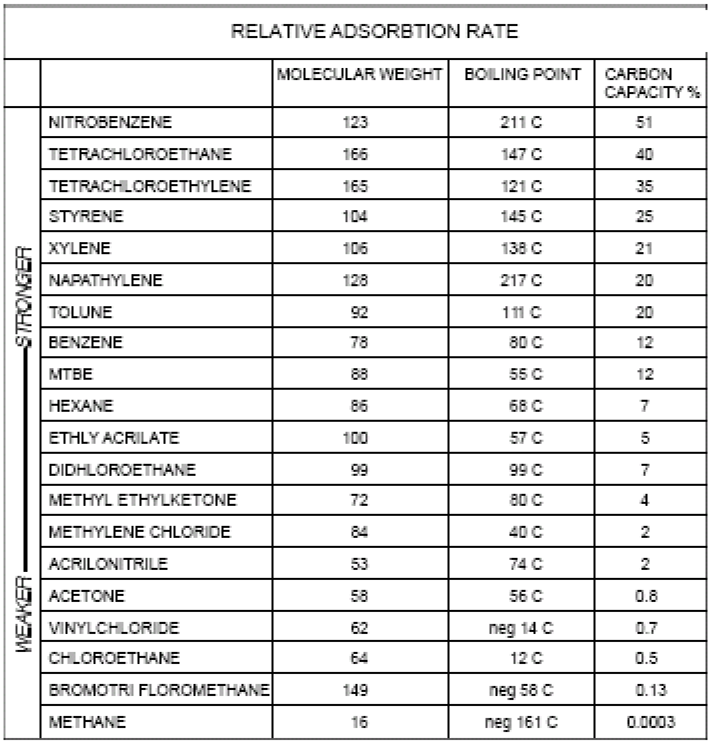
Table 15: Physical Properties of AC

Density	350	kg/m^3
Surface Area	500	m^2/g
Cost 1	$4	per kg

*(http://www.activated-carbon.com/1-3.html)

In addition, activated carbon adsorbs VOCs by the following amounts:

Table 16: AC Adsorption of certain compounds

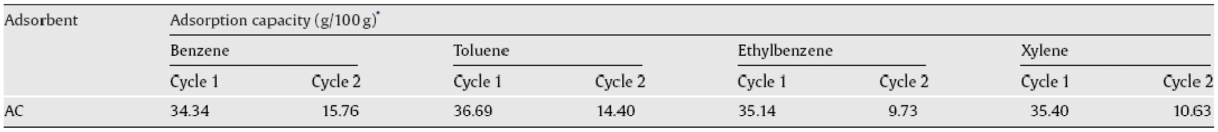


RELATIVE ADSORBTION RATE				
		MOLECULAR WEIGHT	BOILING POINT	CARBON CAPACITY %
WEAKER——STRONGER	NITROBENZENE	123	211 C	51
	TETRACHLOROETHANE	166	147 C	40
	TETRACHLOROETHYLENE	165	121 C	35
	STYRENE	104	145 C	25
	XYLENE	106	138 C	21
	NAPATHYLENE	128	217 C	20
	TOLUNE	92	111 C	20
	BENZENE	78	80 C	12
	MTBE	88	55 C	12
	HEXANE	86	68 C	7
	ETHLY ACRILATE	100	57 C	5
	DIDHLOROETHANE	99	99 C	7
	METHYL ETHYLKETONE	72	80 C	4
	METHYLENE CHLORIDE	84	40 C	2
	ACRILONITRILE	53	74 C	2
	ACETONE	58	56 C	0.8
	VINYLCHLORIDE	62	neg 14 C	0.7
	CHLOROETHANE	64	12 C	0.5
	BROMOTRI FLOROMETHANE	149	neg 58 C	0.13
	METHANE	16	neg 161 C	0.0003

*(Shepherd (2001))

BTEX is on the high end of adsorption available for activated carbon. Activated carbon must be replaced after 2 runs due to low regeneration ability. This regeneration and adsorption after can be represented by the following table:

Table 17: Absorption of AC after 1 cycle regeneration



Adsorbent	Adsorption capacity (g/100 g)*							
	Benzene		Toluene		Ethylbenzene		Xylene	
	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 1	Cycle 2
AC	34.34	15.76	36.69	14.40	35.14	9.73	35.40	10.63

*(Standecker (2008))

In order to evaluate the cost, the amount of absorbent to remove concentrations of BTEX from a Milago type plant for natural gas flow from 575MMSCFD is calculated. This mass of adsorbent was then evaluated as cost of the absorbent to run the two pressure swing adsorption columns in

12 hour intervals. There was an assumption of lowering the pressure of the column not being currently used to atmospheric pressure in order to de-adsorb the BTEX from each column. This was then sent to one of two designs. The schematic for this setup is as follows:

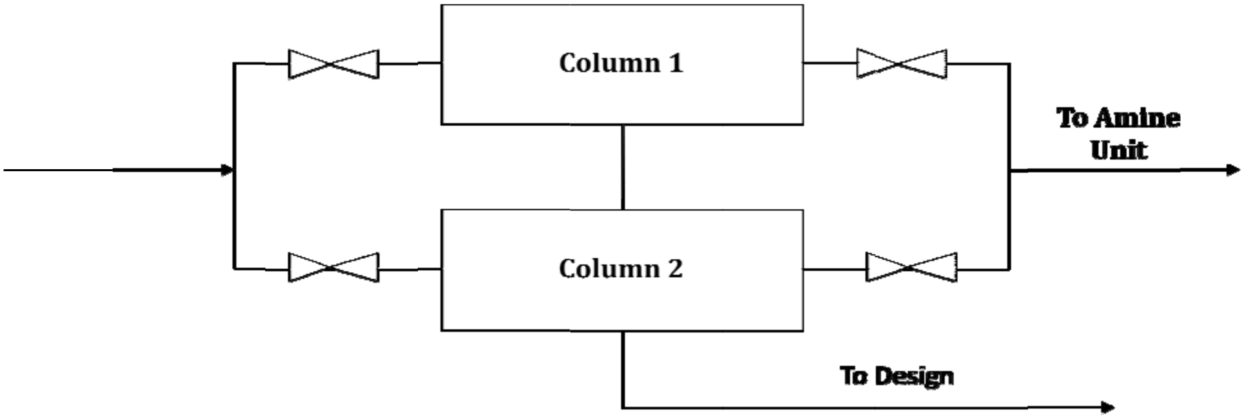


Figure 23: System Setup for Silica Aerogels

This system will then be sent to a possibility of two separate designs. These designs are shown in figures 24 and 25.

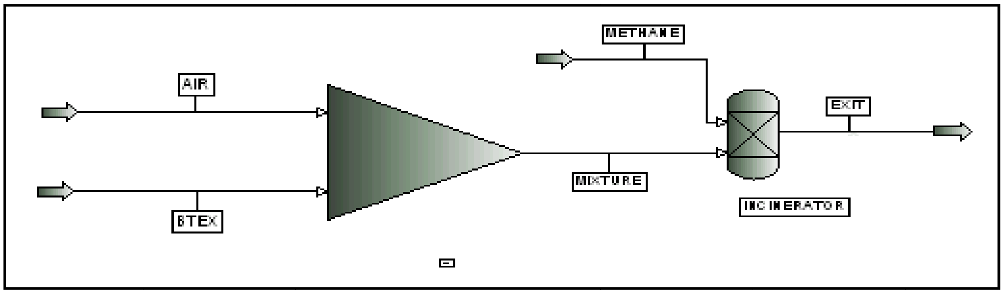


Figure 24: Design 1

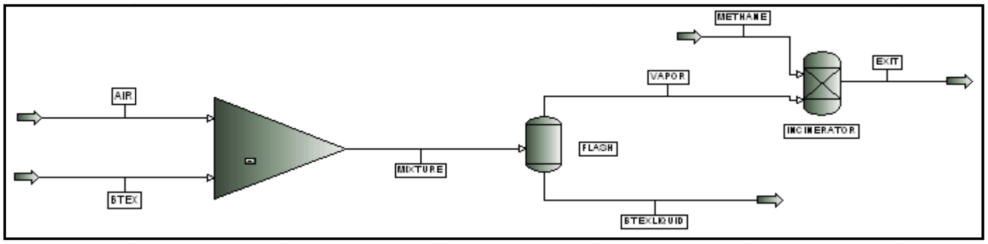


Figure 25: Design 2

Design 1 consists of desorbing of BTEX in a 12 hour period by a simple temperature release in the case of acid gas and a pressure release in case of feed gas. This BTEX is then mixed with enough air to be in vapor form. This mixture is then mixed with methane (fuel) into the oxidizer or flare and raised to 1500°F to incinerate BTEX.

Design 2 is the same concept, except that after mixing the temperature is dropped right below the dew point and some of the BTEX is retrieved. This mixture is then flashed and the vapor is mixed with methane (fuel) in the oxidizer. This combustion occurs at 1500°F.

The columns were priced and sized using the amount of adsorbent needed +10% in order to compensate any absorbent lost during the adsorption and desorption process. The formula for this material is represented below:

$$\frac{lb-mol\,inlet\,gas}{hr}*\frac{453.6\,g-mol}{lb-mol}*\frac{24\,hour}{day}*\frac{X\,mol\,ethylbenzene}{1000000\,inlet}*\frac{106.167\,grams}{g-mol\,EB}*\frac{100\,g\,adsorbent}{93.98\,EB}*\frac{1\,kg}{1000\,grmas}$$

$$\frac{Ads\,kg}{day}*\frac{day}{212-hour}*\frac{2\,columns}{}=\frac{Ads\,needed}{day}*\frac{day\,of\,Ads}{last\,week}*\frac{52\,weeks}{years}*\frac{\$37}{kg}*1.2\;for\,10\%\,extra=\frac{\$SAG}{year}$$

Once the volume needed was obtained the height to diameter ratio of 2-3 was used. This allowed the calculation of the vessel cost (Peters and Timmerhaus, Figure 15-11). The labor was also calculated using the amount of BTEX processed assuming a batch process using Figure 6-9 (P&T). The cost of the blower was done using the flow rate of air needed to bring the desorbed BTEX in vapor phase using Figure 12-32 (P&T). The flash tank volume processed was used to size using same figure as the column cost with a 2-3 height to diameter ratio. The piping and instrument cost was based off of 68% of equipment cost as established by Table 6-6 (P&T). The fuel cost was based off $5/MMBtu and 1010 Btu/scf. These designs were compared with that of the extra cost of incinerating at excess temperatures.

The price for activated carbon was found to be $4 per kilogram. In order to estimate worst case scenario of absorption, the aromatic that adsorbed the least was used which is benzene. The following table for the first design was found adding activated carbon in acid gas stream of amine unit:

Table 18: Design 1 Cost for AC

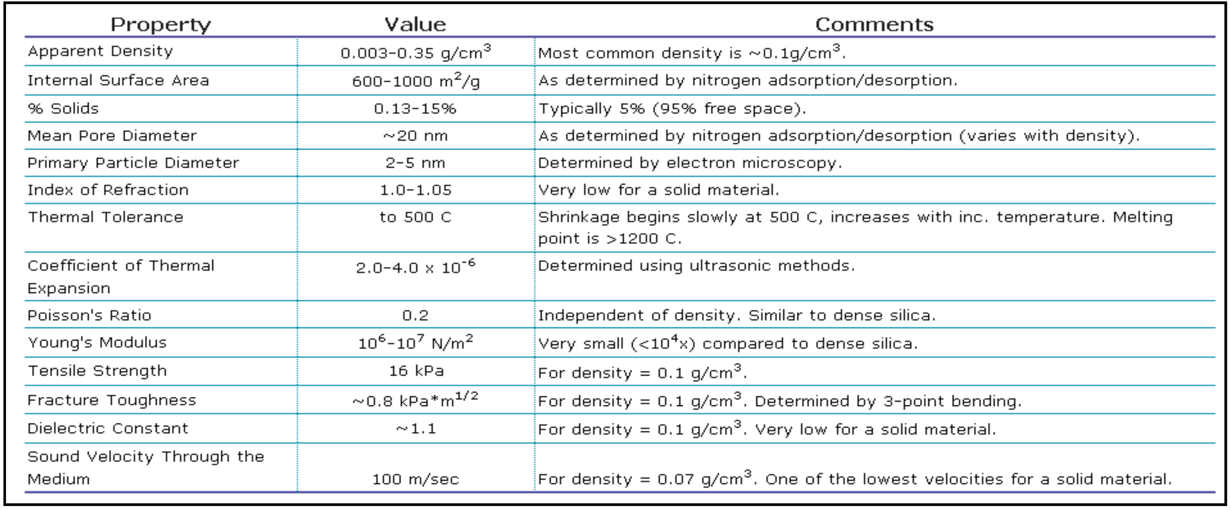
Desorb and Design

Columns	\$372,000
Blower	\$7,000
Piping	\$379,000
Total FCI	\$636,000
Materials	\$257,000
Labor	\$38,000
Fuel	\$5,000
Total Operating Cost	***\$451,000***
Total Annualized Cost	***\$493,000***

The above table shows that the activated carbon would cost \$163,000 more than using incineration at the current price of \$4/kg. In order to save \$100,000, a cost of 22 cents per kg of activated carbon must be used. Since this cost reduction is great, another absorbent such as silica aerogels must be cost analyzed as well.

Use of Silica Aerogels: Silica aerogels (SAG) have emerged in the past five-ten years as a viable adsorbent to separate contaminates from air streams. The physical properties of silica aerogels can be seen below:

Table 19: Physical properties of SAG

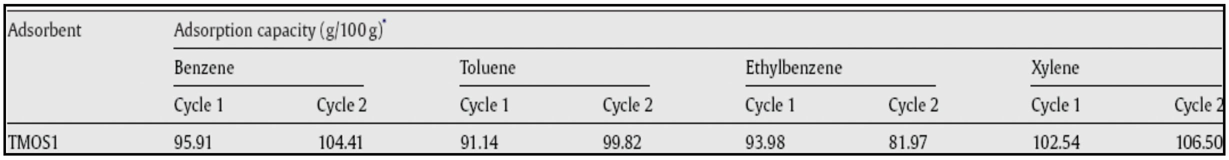


Property	Value	Comments
Apparent Density	0.003-0.35 g/cm^3	Most common density is ~0.1g/cm^3.
Internal Surface Area	600-1000 m^2/g	As determined by nitrogen adsorption/desorption.
% Solids	0.13-15%	Typically 5% (95% free space).
Mean Pore Diameter	~20 nm	As determined by nitrogen adsorption/desorption (varies with density).
Primary Particle Diameter	2-5 nm	Determined by electron microscopy.
Index of Refraction	1.0-1.05	Very low for a solid material.
Thermal Tolerance	to 500 C	Shrinkage begins slowly at 500 C, increases with inc. temperature. Melting point is >1200 C.
Coefficient of Thermal Expansion	2.0-4.0 x 10^{-6}	Determined using ultrasonic methods.
Poisson's Ratio	0.2	Independent of density. Similar to dense silica.
Young's Modulus	10^6-10^7 N/m^2	Very small (<10^{4}x) compared to dense silica.
Tensile Strength	16 kPa	For density = 0.1 g/cm^3.
Fracture Toughness	~0.8 kPa*m$^{1/2}$	For density = 0.1 g/cm^3. Determined by 3-point bending.
Dielectric Constant	~1.1	For density = 0.1 g/cm^3. Very low for a solid material.
Sound Velocity Through the Medium	100 m/sec	For density = 0.07 g/cm^3. One of the lowest velocities for a solid material.

*(http://eetd.lbl.gov/ecs/aerogels/sa-physical.html)

These gels could be used on natural gas streams for removal of BTEX. Silica aerogels have shown a high proximity for aromatic compounds. The following chart shows how much adsorption of these aromatics can take place per 100 g of SAG:

Table 20: Adsorption capacity of BTEX



Adsorbent	Adsorption capacity (g/100 g)*							
	Benzene		Toluene		Ethylbenzene		Xylene	
	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 1	Cycle 2	Cycle 1	Cycle 2
TMOS1	95.91	104.41	91.14	99.82	93.98	81.97	102.54	106.50

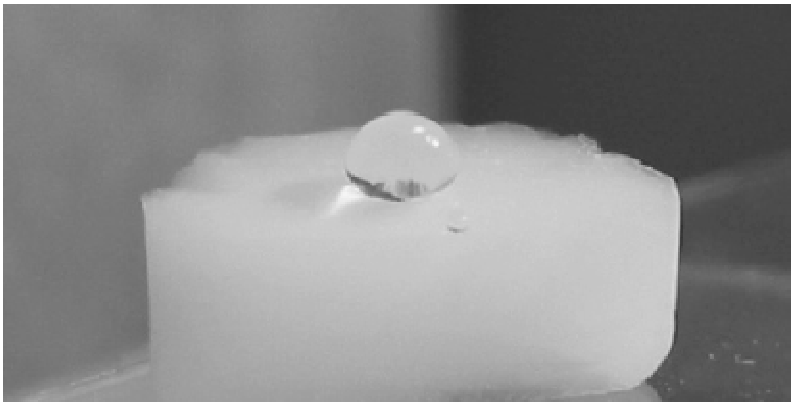
*(Standecker (2008))

We note that silica aerogels have the ability to absorb more BTEX in the second cycle than in the first with all compounds except ethylbenzene. Silica aerogels have also been shown to be reused for up to 14 cycles (Standecker (2008)). In addition, silica aerogels also show low adsorption of other components in natural gas. These adsorptions are as following:

Table 21: Adsorption of hydrocarbons in SAG

Component	Adsorption
Ethane	.02 grams eth/grams SAG
Propane	.07 grams eth/grams SAG

The low adsorption of ethane and propane shows an increase of adsorption as the hydrocarbons increase in number of carbon atoms. This would be that methane would have an even lower adsorption than ethane. In addition, silica aerogels are hydrophobic, meaning they repel water. An example of this can be seen in the TMOS block of SAG with water droplet on it:



*(Standecker (2008))

The way these aerogels are produced have been expensive in the past, but are becoming cheaper to manufacture. The above reactions take place in carbon dioxide enriched atmosphere. This accelerates the formation of the aerogels. One way in which SAGs are produced is the following:

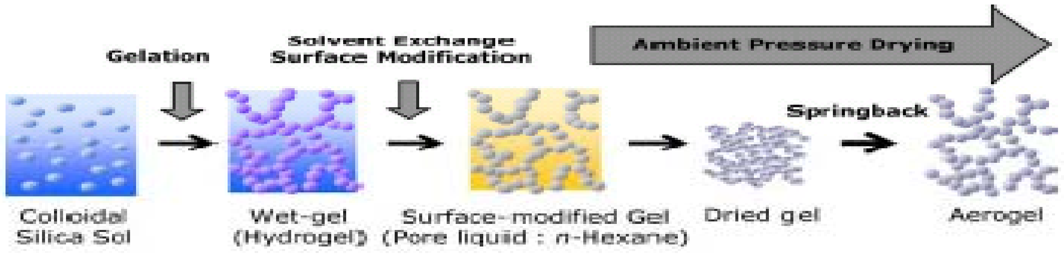


Figure 26: Process of producing SAG *(Hwang (2007))

With such high adsorbent of BTEX, silica aerogels show promise in becoming a cost effective solution in removing BTEX from natural gas prior to processing the gas. The small adsorption of hydrocarbons and zero adsorption of water make SAG usable in natural gas streams. The cost analysis of use of silica aerogels will be reviewed further in the report.

The incineration savings was then used to cost the two designs with the current cost of silica aerogels of $37/kg given by Cabot. This resulted in columns of 3X8m and flash for design 2 of 1X3m. These sizes and cost were done using Peter & Timmerhaus using Marshall and Swift Index to cost the equipment at a today price. The cost results are as follows:

Table 22: Design 1 Cost for 7 cycles at $37/kg

Desorb and Burn		
Columns	$384,000	
Blower	$7,000	
Piping	$226,000	
Total FCI		$657,000
Materials	$1,143,000	
Labor	$38,000	
Fuel	$18,000	
Total Operating Cost		***$1,199,000***
Total Annualized Cost		***$1,240,133***

Table 23: Design 2 Cost for 7 cycles at $37/kg

Desorb and Burn		
Columns	$384,000	
Blower	$7,000	
Piping	$226,000	
Flash Tank	$2,000	
Total FCI		$659,000
Materials	$1,143,000	
Labor	$38,000	
Fuel	*$17,500*	
Total Operating Cost		**$1,199,000**
Revenue	$500	
Total Annualized Cost		**$1,240,000**

As shown above, the cost of both designs exceed saving from lower temperature by about $900 thousand dollars. The distribution of cost can be seen in the following graph based on ppm treated at 500MMSCFD gas flow:

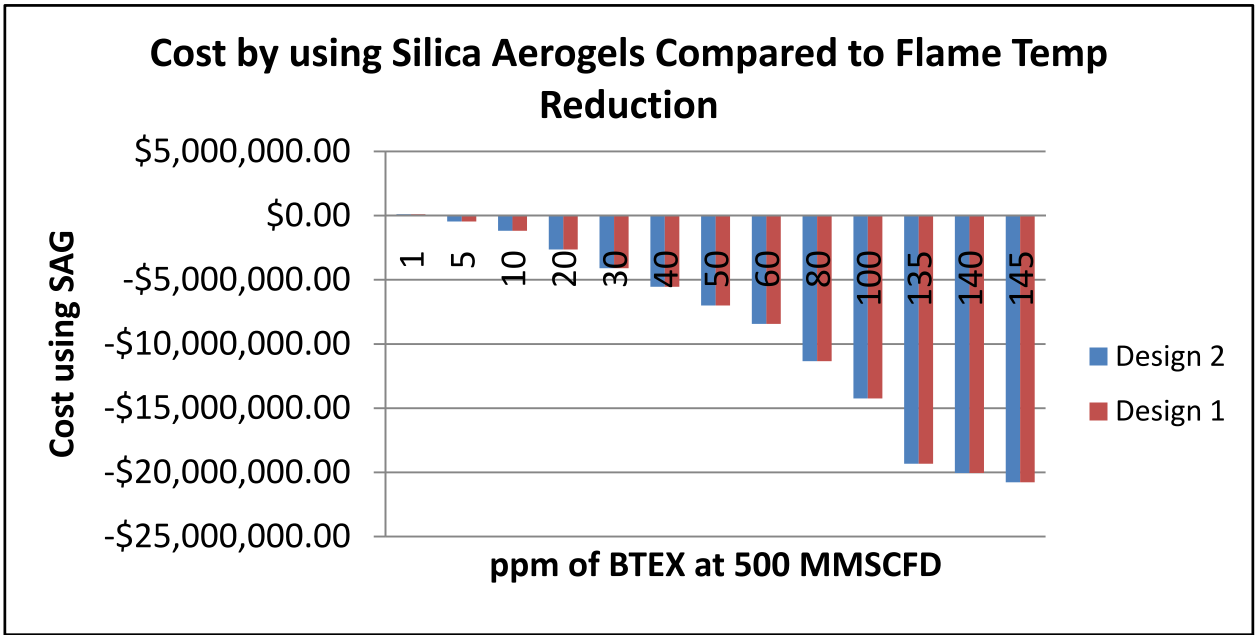


Figure 27: Cost of SAG on different BTEX ppm.

In order to justify using silica aerogels, a reduction of cost per kg will be needed. This can be done with further bulk orders and possible contract with Cabot. The tables for this solved reduce cost is as follows:

Table 24: Design 1 at Reduced SAG Price 14 cycles

Desorb and Burn		
Columns	$384,000	
Blower	$7,000	
Piping	$226,000	
Total FCI		$657,000
Materials	$115,000	
Labor	$38,000	
Fuel	$18,000	
Total Operating Cost		***$170,000***
Total Annualized Cost		***$203,000***

Table 25: Design 2 at Reduced SAG Price 14 cycles

Desorb , Flash, and Burn		
Columns	$384,000	
Blower	$7,000	
Piping	$226,000	
Flash Tank	$2,000	
Total FCI		$660,000
Materials	$114,000	
Labor	$38,000	
Fuel	*$17,500*	
Total Operating Cost		**$170,000**
Revenue	$500	
Total Annualized Cost		**$202,700**

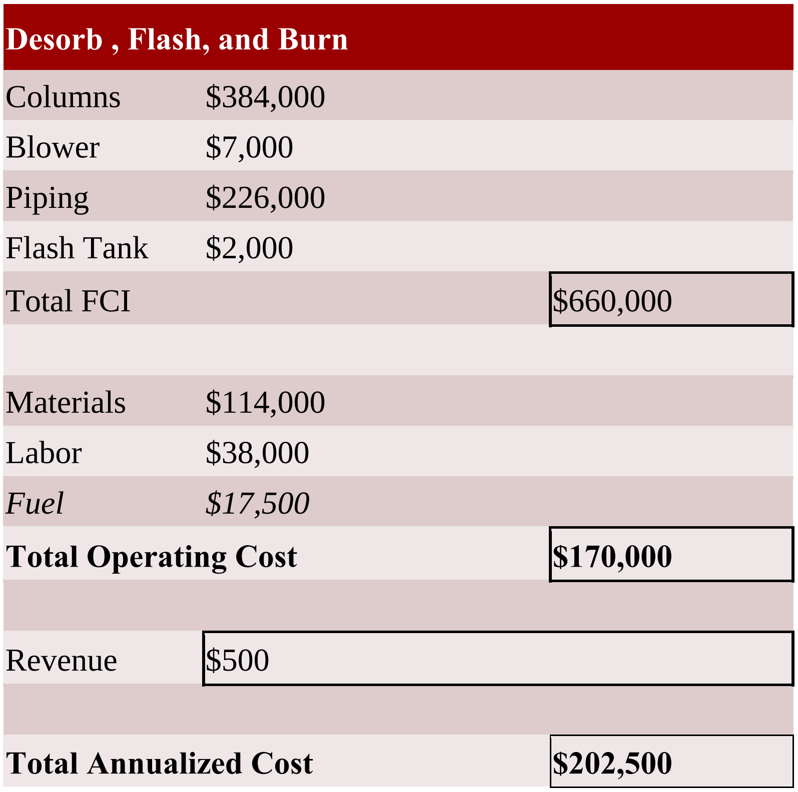
Design 1 would yield a saving of $100,000 per year, and design 2 would yield a saving of $100,300 per year. This cost was found to be about $9 per kg using the 14 cycles instead of 7 cycles.

If we assume the gel has enough adsorption to go 21 cycles without significant losses, the following table would result:

Table 26: Design 1 at Reduced SAG Price 21 cycles

Desorb and Burn		
Columns	$384,000	
Blower	$7,000	
Piping	$226,000	
Total FCI		$657,000
Materials	$115,000	
Labor	$38,000	
Fuel	$18,000	
Total Operating Cost		***$170,000***
Total Annualized Cost		***$203,000***

Table 27: Design 2 at Reduced SAG Price 21 cycles



Desorb , Flash, and Burn		
Columns	$384,000	
Blower	$7,000	
Piping	$226,000	
Flash Tank	$2,000	
Total FCI		$660,000
Materials	$114,000	
Labor	$38,000	
Fuel	*$17,500*	
Total Operating Cost		**$170,000**
Revenue	$500	
Total Annualized Cost		**$202,500**

This would result in a cost of about $14/kg for the cost of silica aerogels.

Considering the low cost of aerogels that must be used in order to meet a $100,000 a year savings, putting such column design in acid gas stream was investigated. The first design of incinerating directly after desorption is the best design for this case, due to the low amount of BTEX in the stream is not enough to make back money from condensing the desorbed vapor. The first trial was run at 7 cycles with a cost of $37/kg. The results for this are as follows:

Table 28: Design 1 Cost in Acid Gas at $37/kg 7 cycles

Desorb and Burn		
Columns	$373,000	
Blower	$7,000	
Piping	$258,000	
Total FCI		$638,000
Materials	$347,000	
Labor	$37,000	
Fuel	$5,000	
Total Operating Cost		***$390,000***
Total Annualized Cost		***$422,000***

By using the aerogels in the acid gas instead of up front of the column, lower flow has to be processed as well as lower amount of BTEX. The data used for these flows and BTEX amount were taken from Pro II simulation from Milagro Plant data. This amounted in an extra cost of $119,000 in comparison with lowering flame temperature. This cost was found using a $37/kg cost of SAG. The optimal cost to save $100,000 was $17/kg.

Below is the same analysis done at 14 cycles with $37/kg:

Table 29: Design 1 Cost in Acid Gas at $37/kg 14 cycles

Desorb and Burn		
Columns	$373,000	
Blower	$7,000	
Piping	$258,000	
Total FCI		$638,000
Materials	$164,000	
Labor	$37,000	
Fuel	$5,000	
Total Operating Cost		***$206,000***
Total Annualized Cost		***$227,000***

This led to a savings of $76,000 per year in savings. In order to reach the $100,000 dollars in savings, a cost of $34/kg is needed.

Below is the same analysis done at 21 cycles with $37/kg:

Table 30: Design 1 Cost in Acid Gas at $37/kg 21 cycles

Desorb and Burn		
Columns	$373,000	
Blower	$7,000	
Piping	$258,000	
Total FCI		$638,000
Materials	$115,000	
Labor	$37,000	
Fuel	$5,000	
Total Operating Cost		***$158,000***
Total Annualized Cost		***$190,000***

This leads to a savings of $143,000 per year for 21 cycles at $37/kg.

Due to the savings possible by implementation of silica aerogel columns in acid gas streams, these columns should be looked at it as a possible solution to BTEX emission issues.

Use of Macroreticular Resins: Macroreticular resins have shown signs of selectivity of BTEX in adsorption columns. These columns adsorption of BTEX can be seen in Langmuir factors below:

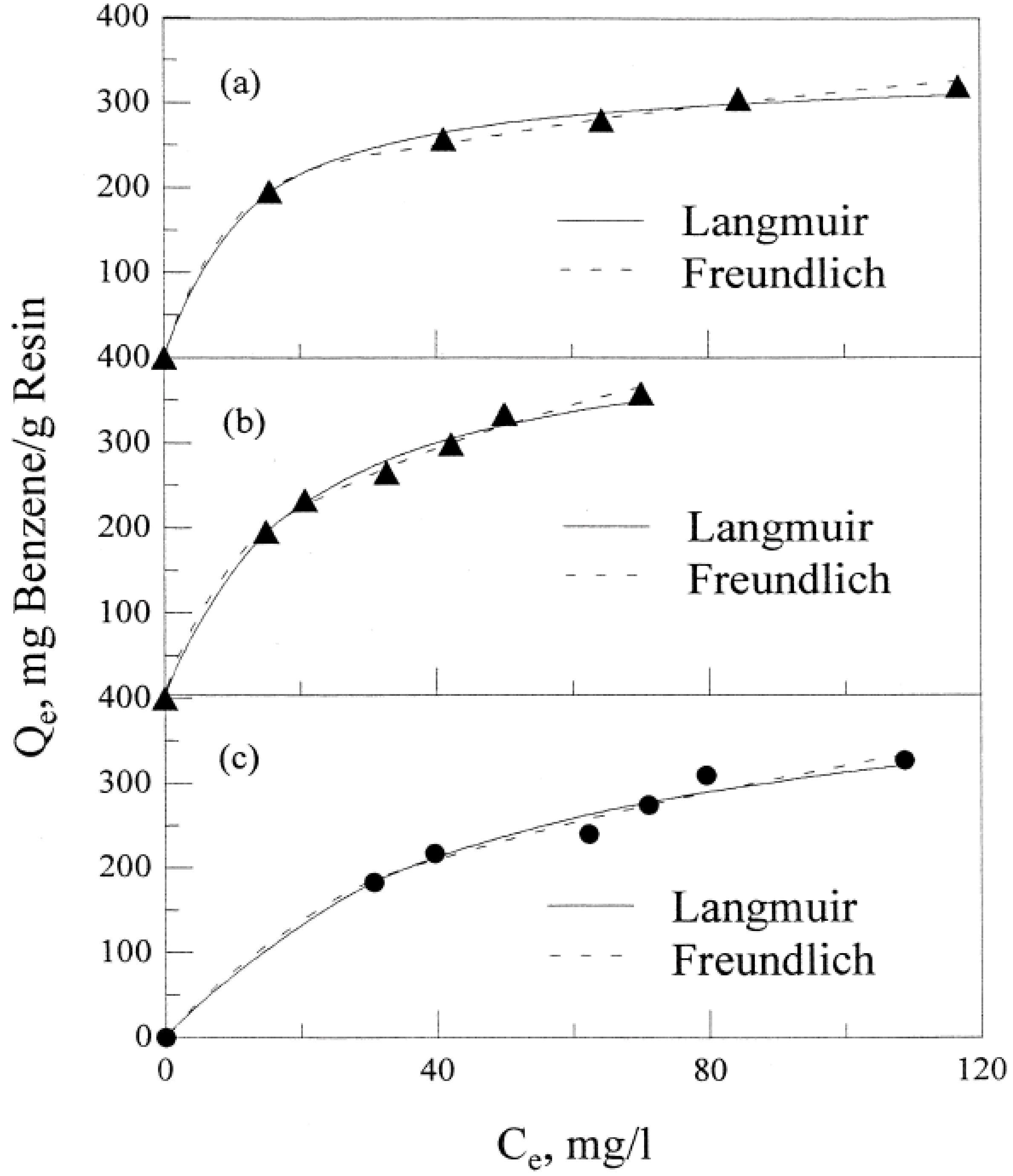
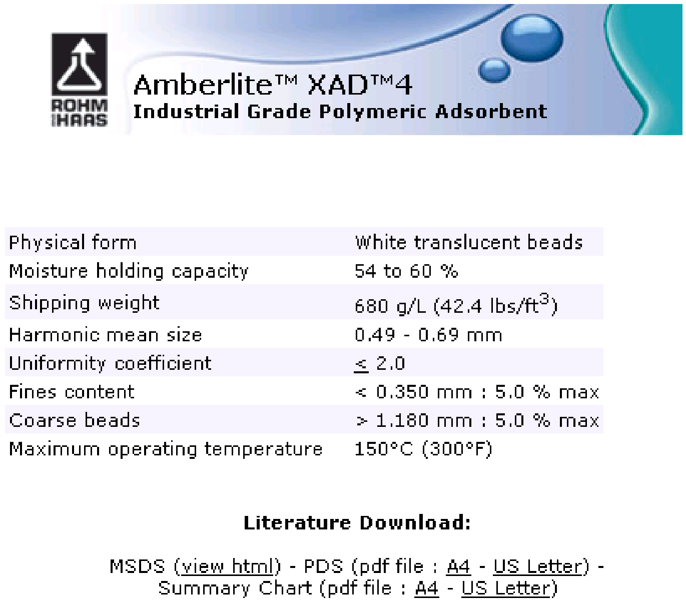


Fig. 6. Comparison of the model fit of benzene adsorption isotherms by Ambersorb 563 (a), 572 (b) and 600 (c) with 0.5 g adsorbent and at 30°C.

Figure 28: Adsorption Langmuir of Benzene on Ambersorb ions (Lin, 1999)

These adsorption isotherms are similar to those of the Amberlites, Amberlite XAD4, a product of ROHM & HAAS, subsidiary of DOW, has the highest selectivity towards BTEX. The physical properties of this ion exchange resin can be seen below:



Amberlite™ XAD™4

Industrial Grade Polymeric Adsorbent

Physical form	White translucent beads
Moisture holding capacity	54 to 60 %
Shipping weight	680 g/L (42.4 lbs/ft^3)
Harmonic mean size	0.49 - 0.69 mm
Uniformity coefficient	≤ 2.0
Fines content	< 0.350 mm : 5.0 % max
Coarse beads	> 1.180 mm : 5.0 % max
Maximum operating temperature	150°C (300°F)

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MSDS (view html) - PDS (pdf file : A4 - US Letter) -
Summary Chart (pdf file : A4 - US Letter)

Figure 29: Physical Properties of Amberlite XAD4 (DOW)

In addition to this, these have shown to lose 5% adsorption capacity after 20 cycles (Chen (1990)). This allows for the product to be used for up to 40 cycles without a major loss in adsorption of 10%.

The same procedure for the silica aerogels and activated carbon was used on the resins. These resins turned to have lower adsorption ability and higher initial cost which results in the following table:

Table 31: Design 1 Cost in Acid Gas at $42/kg 42 cycles

Desorb and Burn	
Columns	$165,000

Blower	$7,000	
Piping	$117,000	
Total FCI		$289,000
Materials	$181,000	
Labor	$37,000	
Fuel	$5,000	
Total Operating Cost		***$223,000***
Total Annualized Cost		***$242,000***

This would have a savings of $61,000 in comparison to incinerating at higher temperature. In order for this to save $100,000 a year, price reduction to $35/kg would need to be arranged with Dow Chemical.

CONCLUSIONS

Three possible solutions in removing BTEX from amine plant acid gas emissions were researched. These included minimizing absorption in the amine, removing within amine unit, or removing before amine unit.

The first option is one of the least viable options due to minimizing BTEX absorption in the amine unit only sends the BTEX problem downstream. This would not be bad if tweaking the parameters of the amine unit only affected BTEX. It could have a similar affect on the absorption of carbon dioxide and hydrogen sulfide too.

The second option of removing BTEX within the amine unit can lead to similar issues as removing it minimizing the absorption in the unit. In order to use this technique of removing within unit, maximizing the absorption would have to be achieved by tweaking parameters. This would in turn affect the absorption of carbon dioxide and hydrogen sulfide. This type of removal could also result in loss of amines due to adsorption into a column costing extra to produce correct weight percent of the amine.

The third option of removing BTEX prior to entering column consist of looking into use of solvents such as water and adsorbents such as activated carbon, modified sand, and silica aerogels. As explained earlier, high flow rates of water are needed in order to separate BTEX from the natural gas. In addition, an adsorbent would be needed to separate the BTEX from the water. The water also has competing adsorption of hydrocarbons such as methane with Henry constant almost 100 times that of benzene. This competition would lead to methane loss, which affects price of gas sold. The use of modified sand shows promise but is used mostly in the case of liquid adsorption of BTEX. This becomes less useful for removing in natural gas unit. The use of solvent such as water added more cost since separation after dissolving BTEX in solvent would be needed. This extra cost led adsorption to be the front runner. The adsorption solutions consisted of using activated carbon, silica aerogels, and macroreticular resins.

All three adsorbents were priced as two pressure swing adsorption columns. With the current prices of AC, SAG, and ionic resins, activated carbon appeared to be clear solution. This was not the case since silica aerogels showed a 6 times better adsorption rate then did activated carbon while seemed to be the worse.

The use of AC showed an extra price of over $163 thousand in comparison to incineration when system was placed in acid gas stream of gas plant with 8 ppm BTEX and flow of 575 MMSCFD. This led to activated carbon being discarded as a possibility.

Overall pricing of the SAGs in comparison to incineration cost led to a cost being able to treat about a plant with 8 ppm BTEX inlet at a flow of 575MMSCFD to be more expensive then incineration in the front of the unit. When the column was placed at the back of the unit, this savings was easily made $100,000 by simply reducing cost of gels from $37/kg to $34/kg. Due to contacts made with Cabot Corporation, higher concentrations of BTEX could be treated if contracts and bulk discounts were discussed.

The pricing and lower adsorption of ionic resins led to the assumption of not a possible solution. However, macroreticular resins showed promise in being able to perform 42 cycles without significant reduction in adsorption, less than ten percent. This led to a saving in the acid gas of $100,000 by reducing the original price of resins from $43/kg to $35/kg. This might be possible through DOW but not as certain as Cabot.

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