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Methanol distribution in amine systems and its impact on plant performance

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Abstract:

Methanol injection into natural gas streams is commonly used to prevent hydrate formation and icing. Downstream, when the gas is scrubbed, the residual methanol enters and tends to build up in the amine treating system. Aqueous amines tend to absorb methanol present in the feed gas. This increases the solubility of other hydrocarbons and affects acid gas vapor-liquid equilibrium. Additionally, significant amounts of methanol then enter in the acid gas fed to the sulfur unit, causing catalyst degradation, lower sulfur recoveries and higher sulfur emissions. Existing simulation tools do not allow for rigorous simulation of methanol in amine systems. Recently, we introduced the ability to simulate methanol in amine systems on a mass transfer rate basis. This paper details how methanol distributes in amine systems, and it quantifies its effect on reboiler energy usage in a typical amine unit.

Methanol in gas treating

Methanol is injected into pipeline gas from natural gas wellheads to control hydrate formation and icing. When natural gas has to be treated for removal of carbon dioxide (CO₂) or hydrogen sulfide (H₂S), methanol injected upstream enters the amine system. Since methanol is a polar compound, aqueous amines have an affinity and tend to absorb methanol present in the feed gas. Consequently, it is necessary to understand how and where the methanol is distributed in the amine unit treated gas, flash gas, reflux purge, and acid gas streams. Figure 1, is a typical amine flowsheet, where the common points of interest of methanol distribution are marked.

Methanol impact on downstream units

Methanol affects downstream processing in units such as sulfur recovery, and natural gas liquids recovery (NGL). In the case of sulfur recovery, methanol causes premature catalyst degradation, leading to lower sulfur recovery, increase in combustion air requirements, reduced hydraulic capacity, and higher sulfur emissions. For NGL recovery, excessive methanol ends up in the NGL product. In addition, methanol also affects volatile organic compound (VOC) emissions which has substantial environmental and economic impact on operations of gas processing plants.

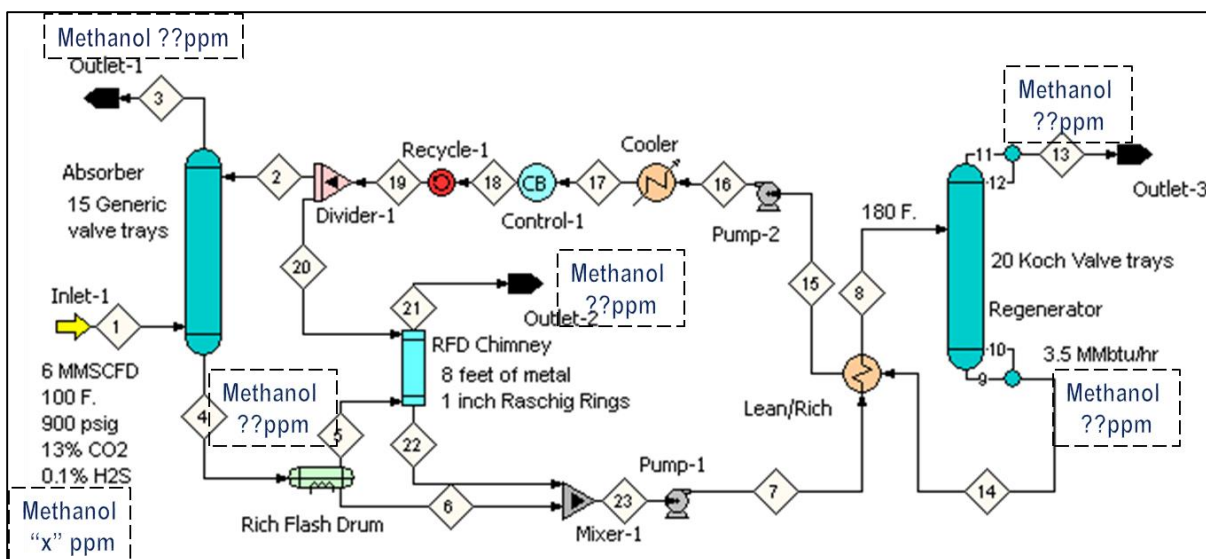


Figure 1: Points of interest for methanol distribution in a typical amine unit, when methanol is present in the feed gas

Methanol properties

Table 1 below is a summary of the properties of methanol that are relevant in amine treating units. Methanol has a vapor pressure that is much higher than water, but lower than ammonia. Additionally, methanol is a polar compound and is completely soluble in water. The complete solubility in water and strong polarity cause the methanol to leave with the amine solution in the absorber. Despite its higher volatility, stripping methanol out of solution in the stripper is a challenge because of its high solubility in the amine.

Table 1: Properties of Methanol

Property	Quantity
Vapor Pressure at 20°C (kPa)	13.02 (2.33 for water, 857.1 for Ammonia)
Boiling point (°C)	64.7
Polarity	5.1 (10.1 for water, 0.0 for alkanes)
Solubility in water (%)	100
Heat of Vaporization at 64°C (kJ/mol)	35.3

Typical Amine Unit Simulation

Case 1: Feed Gas with 0.1% H₂S and 13% CO₂ and high pressure (900 psig)

ProTreat® rate-based mass transfer simulation software was used to model the fate of methanol within the amine unit when about 20 ppmv of methanol enters the feed gas. In ProTreat, methanol absorption and stripping are simulated on a mass transfer rate basis. Critical process and equipment parameters used for modeling the flow sheet shown in Figure 1 are listed in Table 2 below.

Table 2: Process and Equipment Parameters

Equipment/Stream	Parameter
Inlet Feed Gas	6 MMSCFD at 100°F and 900 psig, with 13% CO ₂ and 0.1% H ₂ S, 80% CH ₄ and 6.9% C ₂ H ₆ , 20 ppmv Methanol
Solvent	MDEA 45 wt%, 50 US gal/min
Absorber	15 generic valve trays, 2 feet tray spacing, single pass, 2.5 inch weir height, 900 psig
Rich Flash Drum Chimney	8 feet of 1 inch metal Raschig rings, 20 psig
Lean/Rich Exchanger	180°F regenerator feed
Regenerator	20 Koch valve trays, 2 feet tray spacing, single pass, 3.0 inch weir height, 15 psig, 3.5 MMBtu/h reboiler duty, 120°F condenser temperature

To understand the impact and the fate of methanol on amine unit performance, flow sheet in Figure 1 was simulated with and without methanol. Table 3 below is a comparison of the absorber performance with and without methanol.

Table 3: Impact of Methanol on Absorber Performance

	With Methanol	No Methanol
Feed gas		
H₂S (mol%)	0.10	0.10
CO₂ (mol%)	13.0	13.0
Methanol (ppmv)	20.0	-
Sweet gas		
H₂S (mol%)	9.49 x 10 ⁻⁶	9.77 x 10 ⁻⁶
CO₂ (mol%)	7.83	7.83
Methanol (ppmv)	0.16	-
Flash Gas		
H₂S (mol%)	3.89 x 10 ⁻⁶	3.89 x 10 ⁻⁶
CO₂ (mol%)	0.12	0.12
Methanol (ppmv)	1.59	-
Lean Amine		
H₂S Loading	3.22 x 10 ⁻⁵	3.31 x 10 ⁻⁵
CO₂ Loading	2.71 x 10 ⁻³	2.70 x 10 ⁻³
Methanol (ppmw)	6.47	-

Rich Amine		
H₂S Loading	7.55 x10 ⁻³	7.55 x10 ⁻³
CO₂ Loading	0.43	0.43
Methanol (ppmw)	22.69	-

From Table 3, it is evident that almost all of the methanol that entered the feed gas is absorbed by the lean amine. Additionally, the presence of methanol did not affect the gas treating in the absorber, with almost no changes to the composition of the sweet gas. Figures 2 and 3, help understand how the methanol is distributed within the absorber itself. The horizontal axis in Figures 2 and 3 is the mole percent of methanol (log scale) and the vertical axis is the segment number within the absorber (number of trays, with tray 1 at the top and tray 15 at the bottom of the absorber). When about 20 ppmv of methanol enters the absorber feed gas at tray 15 at the bottom of the tower, almost all of the methanol is absorbed by the liquid phase before the vapor leaves tray 12 (see Figure 2). As a corollary, in the liquid phase (see Figure 3) the largest change in the methanol composition of the amine happens after tray 12 and lower in the column. Based on the properties of methanol, this behavior of methanol in the feed gas being absorbed by the amine almost immediately on entering the column is not unexpected. Additionally, in Figures 2 and 3, the effect of absorber pressure on methanol is also demonstrated. With decreasing pressure, the amount of methanol absorbed by the amine remains the same (see Figure 3), but the amount of methanol leaving with the sweet gas is higher at lower pressure (see Figure 2). However, the behavior of methanol at all the pressures follows the same pattern – most of the methanol being picked by the amine within the first few trays.

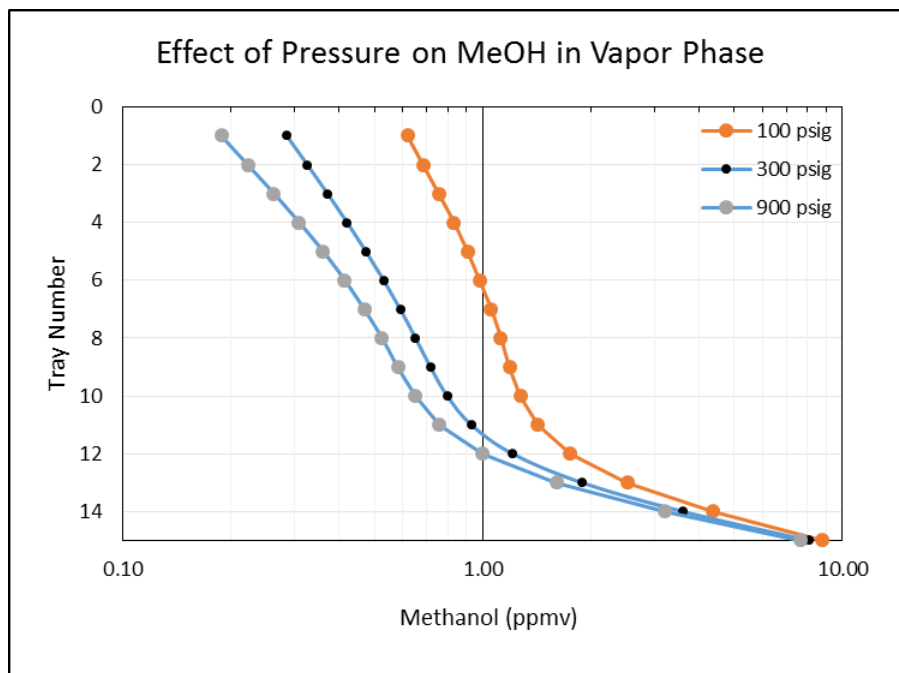


Figure 2: Effect of Pressure on Methanol in Vapor Phase

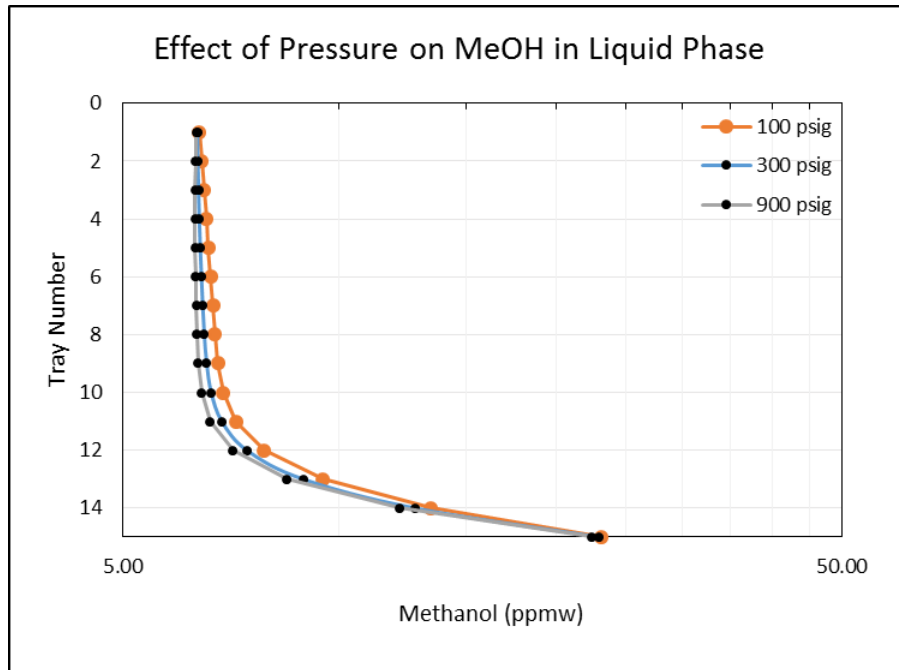


Figure 3: Effect of Pressure on Methanol in Liquid Phase

As a next step, it is necessary to understand the effect of feed gas and amine streams entering the absorber at a different temperatures. Figures 4 and 5, plot the distribution of methanol in the absorber at 100 psig, when the feed gas entered at 100°F and 130°F, while the solvent entered at 110°F and 140°F respectively. At the lower temperature of 110°F solvent, the sweet gas has less methanol (see Figure 4) while the rich amine has higher methanol content (See Figure 5). At the higher temperature of 140°F solvent, the sweet gas has more methanol (see Figure 4) while the rich amine lower methanol content (see Figure 5). Therefore, a higher temperature results in less methanol being absorbed and more leaving with the sweet gas.

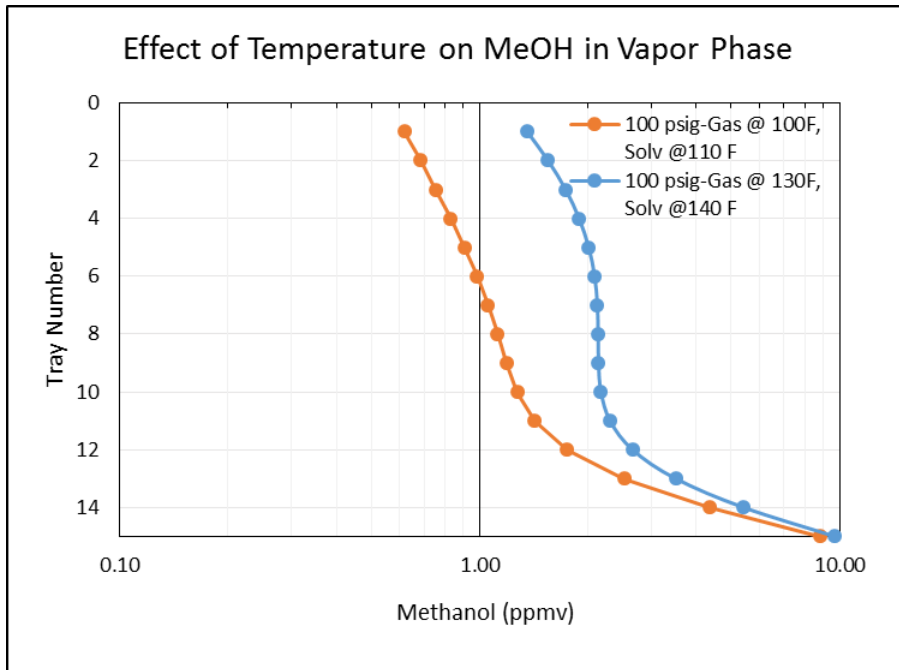


Figure 4: Effect of Temperature on Methanol in Vapor Phase

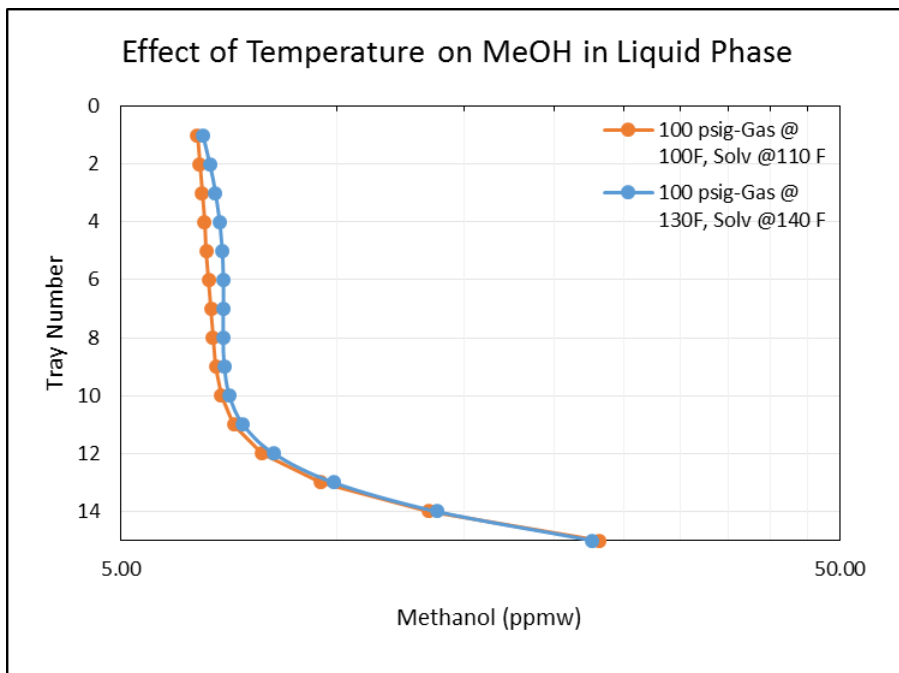


Figure 5: Effect of Temperature on Methanol in Liquid Phase

Table 4 below is a summary of the stripper performance with and without methanol, when the reboiler duty and the condenser temperature were maintained constant. Methanol has almost no impact on the performance of acid gas stripping. When methanol is present, only about 75% of the methanol present in the rich amine is stripped and the remaining continues to be in solution. Figures 6 and 7 are plots of the methanol profiles in the vapor and liquid phase in the stripper.

Notice in the dotted encircled regions of Figures 6 and 7 that, for only 20 ppmv of methanol in the absorbed feed gas, the stripper bulge has about 80 ppmv (0.008 mol%) and the reflux has about 45 ppmv (0.0045 mol%). Despite the high volatility of methanol, the high solubility in the amine limits the ability of the stripper in removing methanol from the rich amine. As a consequence, the stripped solvent still contains about 6 ppmw of methanol (of the 20 ppmv that was absorbed by the lean solvent in the absorber).

Table 4: Impact of Methanol on Stripper Performance

	With MeOH	No MeOH
Rich Amine		
H2S Loading	7.55×10^{-3}	7.55×10^{-3}
CO2 Loading	0.43	0.43
Methanol (ppmw)	22.69	-
Stripped Solvent		
H2S Loading	3.22×10^{-5}	3.29×10^{-5}
CO2 Loading	2.71×10^{-3}	2.70×10^{-3}
Methanol (ppmw)	6.47	-
Heat Duties		
Condenser (MMBtu/hr)	0.81	0.81
Reboiler (MMBtu/hr)	3.50	3.50

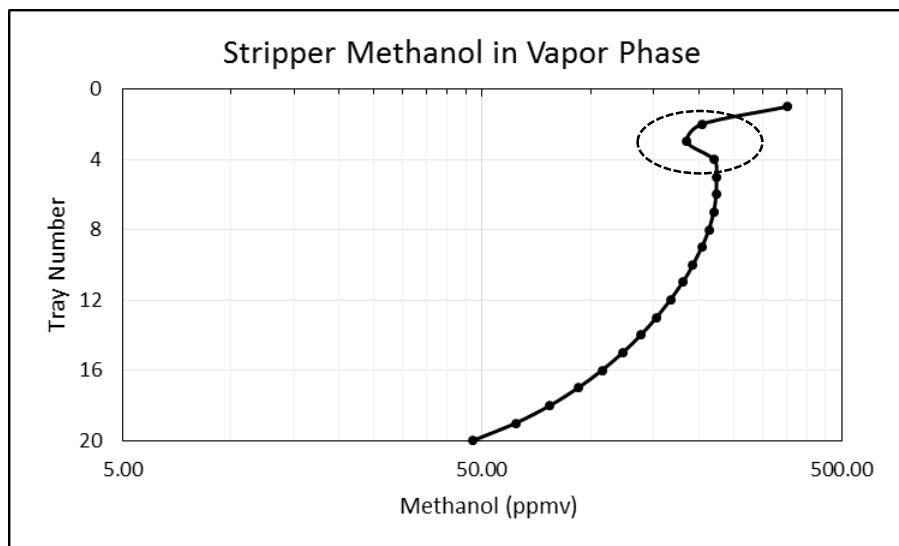


Figure 6: Vapor Phase Methanol Profile in Stripper

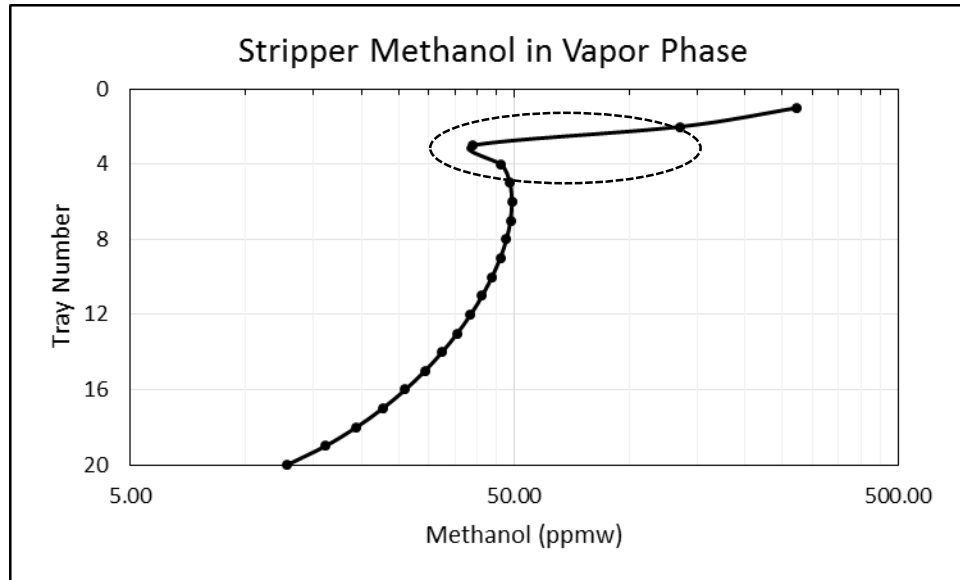


Figure 6: Liquid Phase Methanol Profile in Stripper

Case 2: Feed Gas with 5% H₂S and 1% CO₂ and low pressure (120 psig)

Table 5, below is a summary of the conditions used for Case 2.

Table 5: Process and Equipment Parameters

Equipment/Stream	Parameter
Inlet Feed Gas	6 MMSCFD at 90°F and 120 psig, with 1% CO ₂ and 5% H ₂ S, 87.1% CH ₄ and 6.9% C ₂ H ₆ , varying quantities of Methanol (as shown in Table 2)
Solvent	MDEA 45 wt%, 60 US gal/min
Absorber	15 generic valve trays, 2 feet tray spacing, single pass, 2.5 inch weir height, 120 psig
Rich Flash Drum Chimney	8 feet of 1 inch metal Raschig rings, 20 psig
Lean/Rich Exchanger	210°F regenerator feed
Regenerator	20 Koch valve trays, 2 feet tray spacing, single pass, 3.0 inch weir height, 15 psig, 1lb steam/std US gal reboiler steam flow ratio, 120°F condenser temperature

Table 6, illustrates the impact of varying quantities of methanol in the feed gas at different points in the flowsheet – feed gas, sweet gas and rich amine leaving the absorber, flash gas, lean amine and acid gas leaving the stripper. Based on the sweet gas compositions leaving the absorber in Table 6, it is clear, that there is not significant impact of methanol on the absorber treating. Almost all of the methanol present in the feed gas is picked by the lean amine.

Table 6: Impact of Methanol on Amine Unit Performance for Case 2

	No MeOH	With MeOH				
Feed Gas						
H₂S (mol%)	4.97	4.97	4.97	4.97	4.95	4.94
CO₂ (mol%)	1.00	0.99	0.99	0.99	0.99	0.99
MeOH (ppmv)	0.00	151.76	758.36	1515.56	3780.30	7352.14
Sweet Gas						
H₂S (mol%)	0.01	0.01	0.01	0.01	0.01	0.01
CO₂ (mol%)	0.92	0.92	0.92	0.92	0.92	0.92
MeOH (ppmv)	0.00	6.93	35.48	72.95	207.09	483.16
Rich Amine						
H₂S (loading)	0.38	0.38	0.38	0.38	0.38	0.38
CO₂ (loading)	0.009	0.009	0.009	0.009	0.009	0.009
MeOH (ppmw)	0.00	242.40	1224.09	2476.86	6573.01	14155.85
Lean Amine						
H₂S (loading)	0.01	0.01	0.01	0.01	0.01	0.01
CO₂ (loading)	0.00006	0.00006	0.00006	0.00005	0.00005	0.00005
MeOH (ppmw)	0.00	123.42	631.44	1297.46	3676.70	8546.83
Flash Gas						
H₂S (mol%)	0.007	0.007	0.008	0.008	0.008	0.009
CO₂ (mol%)	0.0004	0.0001	0.0001	0.0001	0.0001	0.0001
MeOH (ppmv)	0.00	23.35	119.54	245.74	697.68	1628.75
Acid Gas						
H₂S (mol%)	91.42	91.29	90.46	89.45	86.44	81.83
CO₂ (mol%)	2.22	2.21	2.19	2.17	2.09	1.98
MeOH (ppmv)	0.00	2488.59	12310.89	24287.29	60139.25	115000.00

The performance of the stripper is further illustrated through Figure 7. From Figure 7, it is evident that with increasing methanol quantities in the feed, the performance of the acid gas stripping seems to be affected adversely. However, one of the interesting things here is that from Table 6, there is significant amount of methanol being recycled back to the absorber in the lean amine. Methanol while being easy to absorb, is not easy to strip. In Figure 7, the horizontal lines (orange for CO₂ and blue for H₂S) correspond to the treating achieved when no methanol was present in the feed gas. At methanol concentrations of 100 ppmv and higher in the feed gas, the mole% of H₂S leaving the stripper decreases. Already, we have seen in case 1 that methanol tends to

accumulate in the stripper causing a stripper methanol concentration bulge in both the liquid and vapor phase. Therefore we really need to understand, what is causing the lower mole% of H₂S to leave from the stripper when increasingly higher quantities of methanol is present in the feed gas.

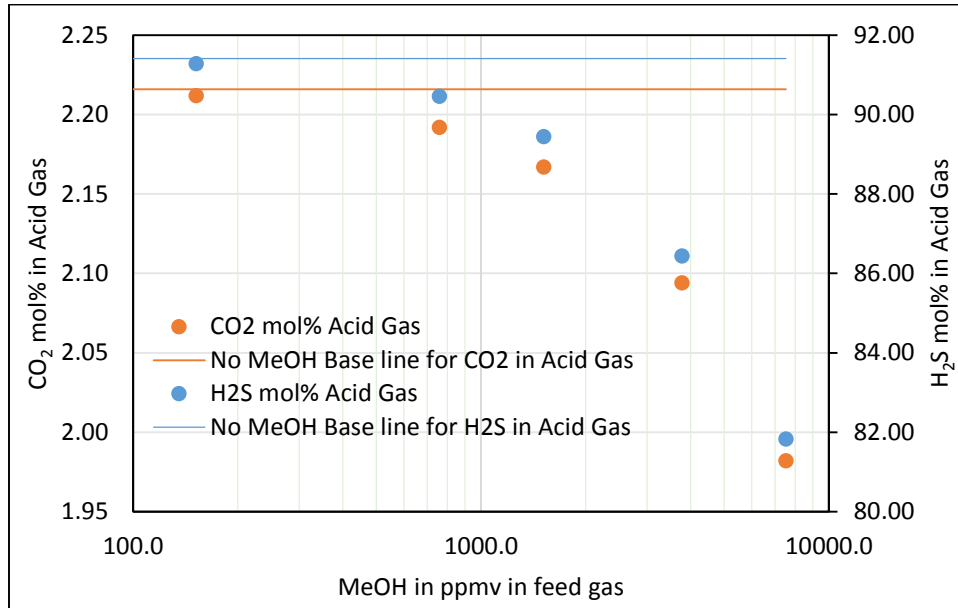


Figure 7: Acid gas leaving the stripper at different feed methanol concentrations

Figure 8 is a plot comparing the flow of H₂S and CO₂ in the stripper with no methanol and with nearly 0.73 mole % (7300 ppmv) in the feed gas. Based on Figure 8, it is clear that methanol is not having any impact as such on the acid gas flow in the stripper, as the profiles of H₂S and CO₂ are nearly the same with and without methanol. The question then remains, as to why the acid gas composition leaving the stripper has lesser H₂S and CO₂. To understand this we need to look at Table 7, the molar flows of the acid gas in the rich amine, lean amine and acid gas, with and without methanol. From Table 7, we make an important observation that the quantities of H₂S being absorbed and stripped remains almost the same, from no methanol to as much as 0.73 mol% of methanol in the feed gas. Therefore, the excess methanol present in the feed gas, and picked up by the lean amine, makes for significant vapor-liquid traffic in the stripper. Additionally, methanol tends to accumulate in the stripper, causing a large quantity to be released with the acid gas, thereby lowering the “purity” of the acid gas leaving the stripper. When significant amounts of methanol are present in the rich amine, the reboiler heat duty (if set to steam flow ratio control) will go up in order to continue stripping the acid gas from the amine at the same level (as when no methanol was present). Simulated test experiments reveal that when methanol is “artificially” added to the rich amine entering the stripper, the increase in the reboiler duty is a function of the amount of methanol “artificially” added.

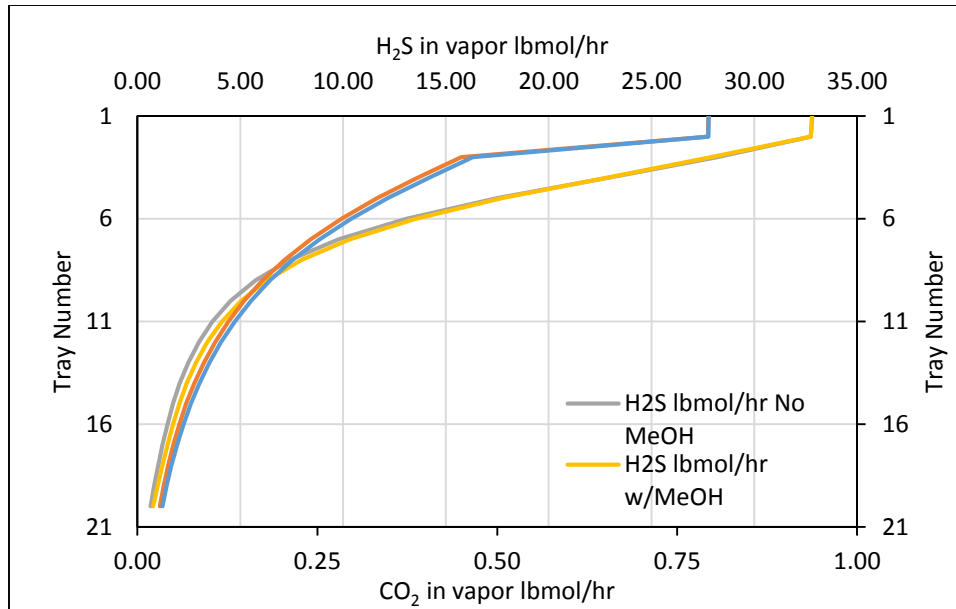


Figure 8: Impact of Methanol on Acid Gas Profiles in the Stripper

Table 7: Amounts of H₂S Absorbed and Stripped

	No MeOH	With MeOH				
Rich Amine						
H₂S(lbmol/hr)	33.4	33.4	33.4	33.4	33.4	33.4
Lean Amine						
H₂S(lbmol/hr)	0.884	0.886	0.894	0.905	0.942	1.010
Acid Gas						
H₂S(lbmol/hr)	32.7	32.7	32.7	32.7	32.7	32.7

Conclusion

This paper demonstrates the impact of methanol on a typical amine unit using rate based simulation software. The performance of the absorber and stripper, in terms of acid gas treatment, is not significantly affected by the presence of methanol. Almost all of the methanol entering the absorber feed gas is absorbed, with temperature and pressure having negligible effects on the methanol pick up by the lean solvent. The amount of acid gas picked up by the lean solvent itself is unaffected by the presence of methanol, but methanol accumulation in the stripper dilutes the composition of the acid gas leaving the stripper. Also, in the stripper, only about 75% of the methanol is stripped from the solution, despite its high volatility, due to methanol's high solubility in the amine. There is also a rather large methanol bulge on a stripper, below the feed tray. Further, at this point, there is no data that exists to suggest that the methanol accumulation in the stripper causes a driving force to hold heavier hydrocarbons in solution. The industry will do well by working on collecting experimental equilibrium data with methanol in amine systems, and the impact that methanol has on acid gas loadings as well as hydrocarbon co-absorption. Also

sampling amine units at points of interest will provide the industry with data to further substantiate the fate of methanol that enters the absorber feed gas.