The CONTACTOR™

Published Monthly by Optimized Gas Treating, Inc.
Volume 9, Issue 9, September, 2015

Dealing with Methanol in an Amine Unit

Methanol (MeOH) is on EPA's list of Hazardous Air Pollutants and is frequently injected into natural gas streams to prevent hydrate formation in gas transmission lines. Later, when the gas is scrubbed, the residual MeOH enters and may build up in the amine treating system. Aqueous amines tend to absorb methanol present in the feed gas which may affect acid gas vapor-liquid equilibrium. Additionally, significant amounts of MeOH then enter in the acid gas fed to the sulfur unit, possibly causing catalyst degradation, lower sulfur recovery, and higher sulfur emissions. Existing simulation tools do not correctly simulate MeOH in amine systems. Recently, we introduced the ability to simulate methanol in amine systems on a mass transfer rate basis. This issue of The Contactor™ outlines how methanol distributes in amine systems and it examines the effectiveness of a water wash upstream of the amine absorber in preventing, or at least reducing, its ingress into the amine system.

Given a certain concentration of methanol in the incoming raw gas, the questions we want to answer are:

- How much MeOH remains in the treated gas and how much absorbs into the rich solvent?
- Can it be effectively removed from the rich solvent in an LP flash?
- How much MeOH remains in the stripped solvent and how much goes overhead with the acid gas to the sulfur plant?

Table 1 shows some important properties of MeOH. It is highly polar and completely miscible in water with a higher vapor pressure than water and a similar boiling point. We expect it will readily absorb.

Table 1 Properties of Methanol

v.p. at 20°C (mm Hg)	97.66 (water is 17.5)
b.p. (°C)	64.7
Polarity	5.1 (water is 10.1)
Water solubility	100%
Latent Heat (cal/mol @ nbp)	8430 (water = 10500)

Case Study

The unit is using 50 gpm of 45 wt% MDEA to treat 6 MMscfd of gas at 100°F and 900 psig. The gas has 13% CO_2, 0.1% H_2S, 80% methane and 6.9% ethane with 20 ppmv MeOH. The absorber contains 15 generic valve trays and, after passing through a flash drum and chimney with 8-ft of 1-in Raschig Rings at 20 psig, the rich solvent is preheated against hot stripped solvent to 180°F. The regenerator uses 20 valve trays and runs at 15 psig with 3.5 MMBtu/h reboiler duty.

This very standard amine treating flowsheet was simulated using the ProTreat® mass transfer rate-based simulator with and without 20 ppmv of methanol in the feed gas to the plant. Table 2 shows how MeOH distributes across various units in the plant and it also shows that methanol itself has only a tiny effect of plant performance from an acid gas removal perspective.

Table 2 MeOH Content of Various Streams

		20 ppmv MeOH	No MeOH
Feed	H_2S (mol%)	0.10	0.10
	CO_2 (mol%)	13.0	13.0
	MeOH (ppmv)	20	0
Sweet	H_2S (ppmv)	0.095	0.098
	CO_2 (mol%)	7.83	7.83
	MeOH (ppmv)	0.16	–
Flash	H_2S (mol%)	0.039	0.039
	CO_2 (mol%)	0.12	0.12
	MeOH (ppmv)	1.6	–
Lean	H_2S (loading)	0.000032	0.000033
	CO_2 (loading)	0.0027	0.0027
	MeOH (ppmw)	6.5	–
Rich	H_2S (loading)	0.0076	0.0076
	CO_2 (loading)	0.43	0.43
	MeOH (ppmw)	22.7	–

Most of the methanol is absorbed, leaving only 0.16 ppmv of the original 20 ppmv in the treated gas. After solvent regeneration, nearly 30% of the absorbed methanol remains in the stripped solvent (6.5 ppmw) and gets recycled back to the absorber.

As shown in Figure 1, absorber operating pressure plays a significant role in methanol removal.

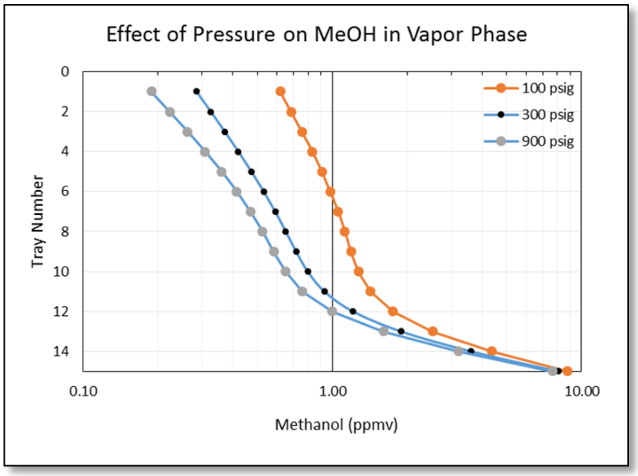

Figure 1 MeOH Removal vs. Absorber Pressure

Methanol shows an interesting concentration bulge just below the feed tray in the stripper (Figure 2). As far as MeOH stripping from the solvent is concerned, this bulge renders about half the trays in the column non-functional.

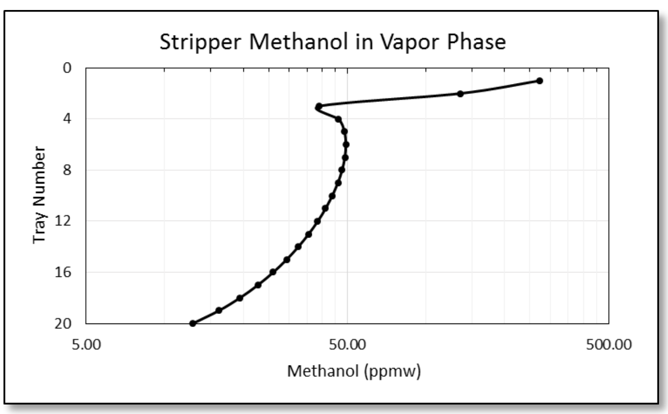

Figure 2 MeOH Concentration in Stripper

If high methanol concentrations are harming sulfur plant catalyst activity, the other question worth asking is whether MeOH can be removed from the gas before it even enters the amine system, perhaps by using a low-flow water wash. The scheme shown in Figure 3 was investigated via simulation.

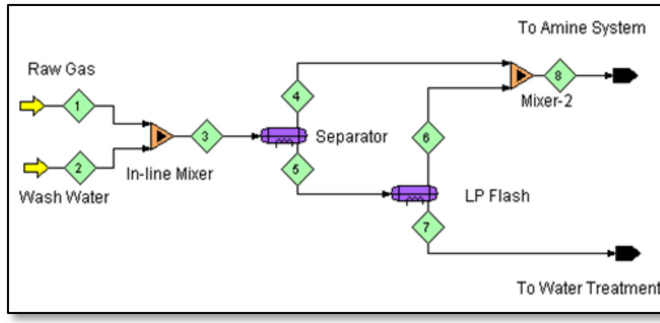

Figure 3 Water Wash Scheme for MeOH Removal

The result of mixing various small volume flows of water with the gas in a motionless in-line mixer and doing a low pressure flash on the water coming from the separator is shown in Figure 4.

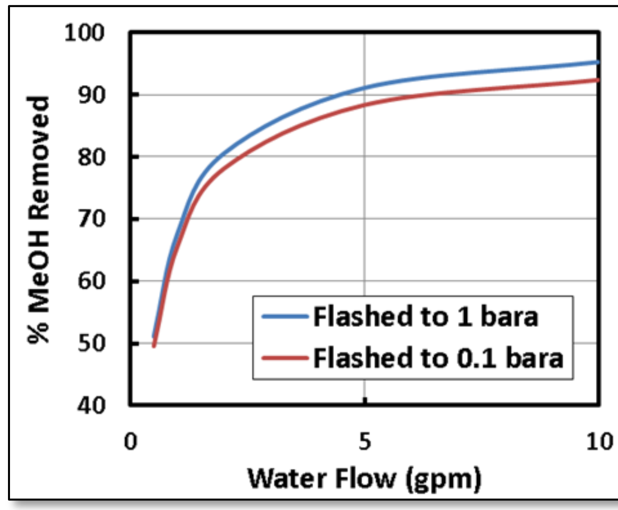

Figure 4 MeOH Removal by Water Wash

Obviously, flashing to atmospheric pressure removes slightly more MeOH than a vacuum flash because less MeOH flashes off and flows to the sulfur plant. The purpose of the vacuum flash, however, is to permit only minimal hydrocarbons loss (< 0.000005% of HCs in the raw gas) and minimal H_2S (< 1 ppmw) in the small wash water stream to the water treatment plant.

ProTreat® mass transfer rate-based simulation has shown where methanol ends up in an amine unit, as well as an unexpected distribution of MeOH within the amine regenerator. Over 95% of the methanol can be removed via a simple, low cost mixer-separator and low pressure flash drum.

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