



## Contaminated Solvents — Methanol in Amine Treating

Hydrate inhibitors used in the gas industry are either methanol (MeOH), or one of the glycols, especially monoethylene glycol (MEG). Methanol is quite effective at preventing the formation of gas hydrates. It is usually mixed with the gas at the wellhead. With a high enough methanol concentration in the water phase, gas hydrates cannot form.

Pipeline plugging must be avoided at all costs. Perhaps for that reason, sometimes grossly excessive amounts of methanol are used “just to be safe”. Apart from the waste associated with high use, none of the added methanol just “disappears”. Except for what is retained as high concentration levels in separations equipment such as absorbers and solvent regenerators, eventually all the methanol ends up in feed streams to various units, and product streams from others. In ethane and propane NGL fractions, methanol is highly undesirable because it negatively affects furnace and converter performance in sulfur plants. When it is realized that if a cracking catalyst is used to convert ethane and propane into ethylene and propylene, only a few 10s of ppmv will poison the catalyst, the importance of keeping methanol usage in check at the wellhead, being able to remove it before it enters processing units or products, and being able to predict where it ends up become obvious.

This issue of The Contactor presents a synopsis of a performance analysis of the CO<sub>2</sub> removal system of one of the many NGL fractionation trains operated by Enterprise Products. The analysis was done using the ProTreat® mass and heat transfer rate-based simulator. Data were collected by Enterprise who also did many of the stream composition analyses. Other stream analyses were done by Dow Chemical.

### Amine Treating Unit

Figure 1 is a schematic of the amine treating unit. The contactor is an in-line static mixer fed by the combined flow of Y-Grade NGL feed and the DEA solvent used for treating. This is followed by a separator-coalescer which splits the mixture into

organic and aqueous phases. The treated liquids pass to a Dehydration unit while the CO<sub>2</sub>-rich amine is regenerated in a conventional reboiled stripper. The question is the fate of methanol.

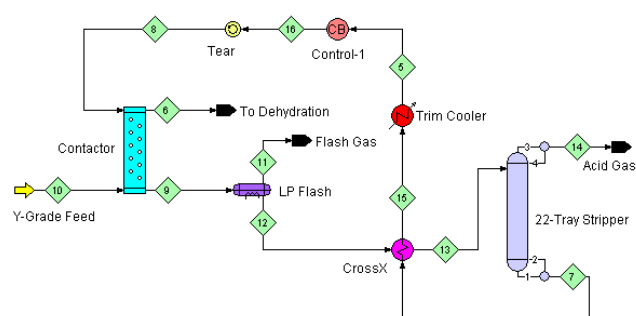


Figure 1 Schematic of CO<sub>2</sub> Treater

In addition to 160 ppmw CO<sub>2</sub> not removed in the original gas treatment step before transporting to the fractionation plant, the NGL also contains 65 ppmw of the original methanol (MeOH) injected into the wellhead gas to prevent hydrate formation. Flow was 3,310 barrels per hour (bbl/h). The MeOH concentration rivals the CO<sub>2</sub> concentration in the Y-grade feed. The solvent concentration was analyzed at 25.4 wt% DEA.

The regenerator was a 22-tray (conventional valve type trays) column operating at approximately 22 psia and with solvent feed to the top tray at 195°F. The reboiler used hot oil and had a known duty.

### Simulation

Initial simulation work was done on the assumption that the static mixer-separator combination acted as a single ideal stage of contact. At all times, however, the regenerator was simulated on a strictly mass transfer rate basis in which methanol and CO<sub>2</sub> stripping were directly determined by their mass transfer rates, not through any kind of ideal stage calculations. The treated NGL composition was simulated to contain less than 1 ppmw of CO<sub>2</sub>, in disagreement with the measured composition of

40–60 ppmw CO<sub>2</sub>. However, when the static mixer was simulated with 62% efficiency, the measured treating levels were reproduced almost perfectly for both components, and the treated NGL contained 63 ppmw MeOH, *almost the same as in the inlet NGL*. One reason for the low efficiency may be the very small amine flow relative to NGL (NGL to amine volumetric flow rate ratio greater than 17:1). This makes the interfacial contact area quite low, making good mass transfer hard to achieve. Other reasons are the low mixing intensity inherent in short motionless mixers, and the low CO<sub>2</sub> content.

Despite ProTreat's known high accuracy in reproducing measured flash gas flows and compositions, the simulated flash gas rate was several times lower than measured. Simulation was done on the assumption of perfect phase separation in the settler. However, in liquid treating the presence of rag layers and the difficulty in removing very fine droplets of one phase from the other are well known. When the simulation was rerun with about 0.08% entrainment of NGL into the amine, the simulated and measured flash gas make rates coincided and, more importantly, *so did the methanol content of the flash gas*.

At this juncture, all other simulated performance parameters were found to be in close agreement with measured data. Methanol, CO<sub>2</sub>, and total flow rate of the acid gas stream from the regenerator were in excellent agreement. Simulated methanol in the lean amine (1.08 wt%) agreed with measured data (0.918 wt%) as well, as did the lean amine loading. More importantly, however, *the methanol contents of the rich and lean amine were virtually identical*. The reason is the condensate returned to the regenerator.

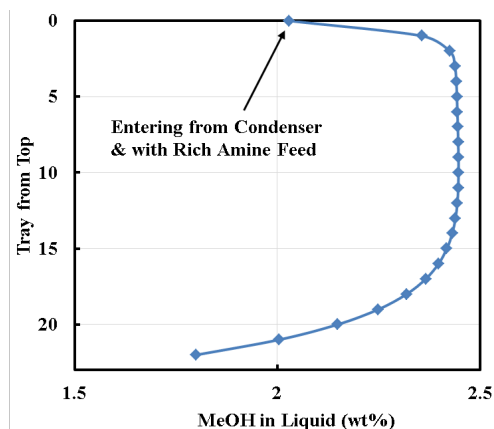
Interestingly, there was a mix up between reflux and lean amine samples, and the laboratory analysis of stripper reflux was reported as 0.7 wt% MeOH. However, the concentration predicted by ProTreat simulation was 19.4 wt%, a huge difference. This led us to resample and reanalyze the reflux water which was found to contain about 17 wt% methanol, in reasonable agreement with the simulation, especially given that the reflux water sample was taken two weeks after the original data were collected.

Of the methanol in the stripper overhead vapor, *fully 99.7% returns to the column in the reflux, and only 0.3% leaves the system with the CO<sub>2</sub> and coabsorbed hydrocarbons*. This might be an excellent place to remove most of the methanol from the system, and incidentally, to remove it from the NGLs, too, because the lean amine could be made very low in methanol, if not virtually methanol

free. Methanol removal is so low because it builds to near equilibrium levels with the treated NGL. It must be bled from the system to remove it. What better place to bleed it than from the reflux via blowdown! Although methanol is quite volatile, it also has a high affinity for water so reflux water is an excellent trap for methanol.

## Methanol Distribution in the Regenerator

Figure 2 shows the simulated methanol distribution across the 22 trays in the regenerator in the amine phase. Each point refers to the stream *leaving* the indicated tray. Only near the bottom of the regenerator does methanol strip from the solvent in a significant way. Indeed, the methanol level on most trays in the stripper is about 25% higher than in the combined reflux and amine feed streams. Near the top of the regenerator the MeOH vapor flow and liquid concentration both drop because of reabsorption of MeOH into the cooler solvent on and near the feed tray.



**Figure 2** Distribution of MeOH in the Amine in the Regenerator

## Summary

Methanol is hard to squeeze from the treating system because of its high affinity for water. Reflux water blowdown appears to offer a simple route to methanol removal from contaminated NGLs and from the circulating amine.

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