

BEHAVIOR AND EFFECT OF METHANOL IN AMINE TREATING SYSTEMS

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ABSTRACT

To prevent the formation of hydrates, methanol is commonly added to well-head gas before it enters pipelines for transport to processing units. Perhaps under the mistaken notion that more is better, copious amounts are sometimes added, amounting to many tons of methanol per day. Almost invariably, a large proportion of the methanol is removed from the gas in the amine unit where it tends to build up to high levels in certain areas, especially in the amine regenerator. Eventually, the absorbed methanol finds its way at high concentrations into the acid gas entering the sulfur plant. There it acts as a diluent, it can seriously lower flame temperatures in the furnace, and it has quite a deleterious effect on Claus catalyst performance. However, not all the absorbed methanol is stripped from the solvent in the regenerator—a sizeable part remains in the lean solvent which returns to the top of the absorber, sometimes causing high methanol levels in the treated gas.

Liquids (NGLs) produced from the treated gas sourced from shale plays, for example, often contain large ethane and propane fractions. These fractions are used as cracker feeds for the production of ethylene and propylene. Methanol is a serious poison to cracking catalysts, so much so that crackers sometime specify zero methanol content in ethane and propane feed stocks, despite the physical and economic impossibility of total removal.

Enterprise Products operates fifteen NGL fractionation trains throughout the United States. This paper reports operating data collected by Enterprise Products from one of these trains. The liquids in the train are first amine treated in separate mixer-settler units to remove residual acid gases, mainly carbon dioxide. Spent amine is regenerated in conventional regenerators. . Samples were analyzed by Enterprise Products and by Dow Chemical. This paper includes comparisons between simulated and measured methanol levels in various locations in the plant. Recommendations to alleviate methanol contamination problem in fractionation train products are made.

INTRODUCTION

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 injected at the wellhead where it mixes with the gas. As the gas flows along a subsea pipeline, for example, it cools (typical seafloor temperature is about 39°F) and free water can start to form, depending on the pressure. At such a temperature, and above a pressure of about 300 psia, hydrate formation is almost assured. As the water condenses, methanol dissolves into it. With a high enough methanol concentration in the water phase, gas hydrates cannot form.

Pipeline plugging must be avoided at all cost. Perhaps for that reason, grossly excessive amounts of methanol are sometimes used “just to be safe”. Apart from the unnecessary cost 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 fractions, methanol plays havoc with catalysts in crackers. In conventional treating of sour gas, it negatively affects furnace and converter performance in sulfur plants. When it is realized that only a few 10s of ppmv will poison the cracking catalysts used to convert ethane and propane into ethylene and propylene, the importance of keeping methanol usage in check at the wellhead, being able to remove it before it enters processing units, and being able to predict where it ends up become obvious.

Ethane and propane can be cracked to ethylene and propylene either thermally (750-900°C) or catalytically (typically 500°C) using a zeolite or other catalyst. Catalytic cracking is done at lower temperatures because it saves a lot of energy; however, unlike in thermal cracking, catalysts are sensitive to, and poisoned by, certain impurities. In particular, methanol is a known catalyst poison. For this reason, ethane and propane fractions intended for cracking have stringent limits on their allowable methanol content.

This paper presents the result of a performance analysis of the CO₂ removal system of one of the 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. Some of the simulation results suggested the contactor performed as less than a single ideal stage, and that there was likely some carry under of hydrocarbon into the rich amine from the contactor. Overall, simulation results compared remarkably well with measured performance data.

AMINE TREATING UNIT

The amine treating unit is shown schematically in Figure 1. The Contactor is an in-line static mixer (also known as a motionless 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 CO₂-rich amine is regenerated in a conventional reboiled stripper. The question is the fate of methanol.

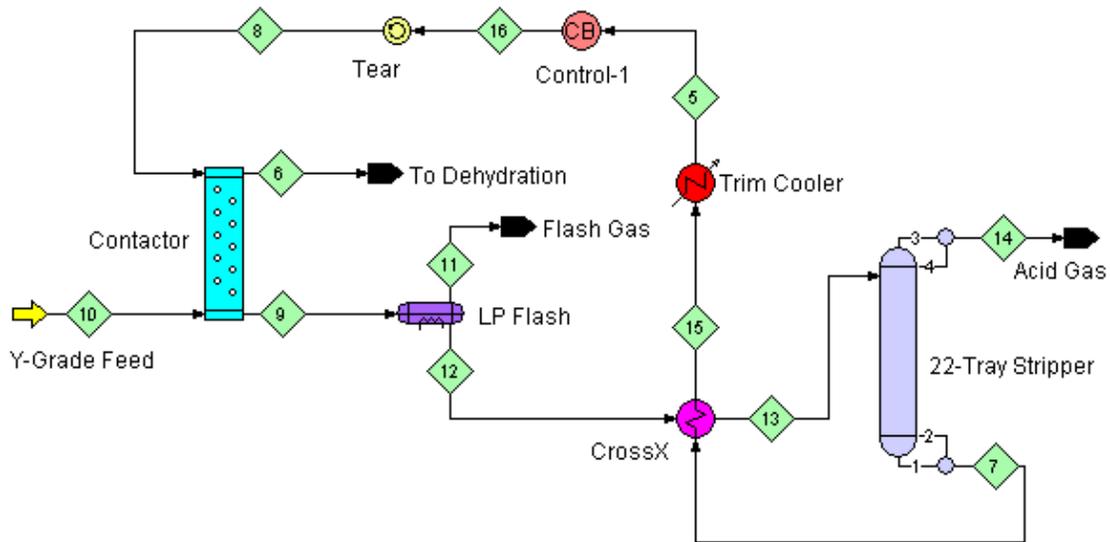


Figure 1 Schematic of CO₂ Treater

Table 1 shows the composition of the NGL feed. In addition to residual CO₂ not removed in the original gas treatment step before transporting to the fractionation plant, the NGL also contains 65 ppmw methanol (MeOH) which remains from the MeOH injected into the wellhead gas to prevent hydrate formation. Flow was 3,310 barrels per hour (bbl/h). The MeOH concentration rivals the CO₂ concentration in the Y-grade feed.

Table 1 Y-Grade Feed Contaminants

| Component | ppmw |
|----------------|------|
| Carbon Dioxide | 160 |
| Methanol | 65 |

The solvent concentration is held within a certain range and was 25.4 wt% DEA as analyzed for this work. It contains 1.25 wt% heat stable amine salts (HSAS). In DEA systems containing anything but the tiniest CO₂ loading, HSAS has no effect on treating *per se* although, of course, they may cause corrosion of carbon steel. The foaming tendency of the lean solvent was classified by Dow as severe. The lean amine was reported to contain 0.92 wt% MeOH.

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 CO₂ 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 CO₂ and only a few ppmw MeOH, in disagreement with the measured composition of 40–60 ppmw CO₂ and several tens of ppmw MeOH. Enterprise suggested that in fact the static mixer-settler unit was performing with efficiency considerable less than 100%, and the rather high residual levels of CO₂ and MeOH were a result of this inherent inefficiency. Indeed, it was found that an efficiency of roughly 60% reproduced the measured treating levels almost perfectly for both components. The primary reason for the low efficiency is the very small amine flow relative to NGL (NGL to amine volumetric flow rate ratio greater than 10)—the interfacial contact area is necessarily small making good mass transfer much harder to achieve. This, combined with the unusually low CO₂ level in the NGL feed (resulting from the high amount of ethane rejection in the field) causes lower efficiency of contact¹.

One of the interesting learnings from the simulation is that both residual CO₂ and the more problematic MeOH levels can be reduced considerably by improving the efficiency of contact with the amine. It does not take a large inefficiency to yield much poorer product quality than can actually be achieved. More intense mixing either by using longer mixers, or multiple units, or by mixer redesign may be a possible way toward significant improvement. On the other hand, more intense mixing may emulsify the hydrocarbon and amine phases, making phase separation more difficult. There is a balance to be struck. Yet another alternative is to recycle part of the amine back to the contactor so that a better volumetric flow ratio of NGL to amine can be achieved, and the interfacial contact area increased.

The simulated flash gas rate was several times lower than measured. Simulation was done on the assumption that the phase separation in the settler was 100%. In liquid treating the presence of a rag layer at interfaces and the difficulty in perfectly removing very fine droplets of one phase from another are well known. When the simulation was rerun with about 0.07% 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. Entrainment of hydrocarbon into the solvent hardly affects treating at all; however, it can have a very significant effect on flash gas rates and it represents an avoidable² loss from the product stream. At the levels present, there may be some impact of the MeOH itself on the solubility of other hydrocarbons in the amine. Previous studies by the GPA ([1], [2]) were with methanol at much lower levels.

At this juncture, all other simulated performance parameters were found to be in excellent agreement with measured data. Simulated methanol in the lean amine and the lean amine loading agreed with measured data. Methanol, CO₂, and total flow rate of the acid gas stream from the regenerator were also in excellent agreement. 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 16 wt%, a huge difference. This led us to resample and reanalyze the reflux water which was then found to contain 17 wt% methanol, in almost perfect agreement with the simulation.

¹ High initial CO₂ means a larger fraction can be removed more easily, although one may still be unable to reach truly low residual levels in the treated NGL stream

² For example, mesh coalescers can effectively prevent entrainment of either phase into the other.

THE FATE OF METHANOL

In a single stage of high efficiency contact, virtually all the CO₂ and most of the methanol can be removed by amine treating. Contactor inefficiencies, however, will result in significant loss of product quality with an unnecessarily large fraction of the methanol in the feed remaining in the product stream.

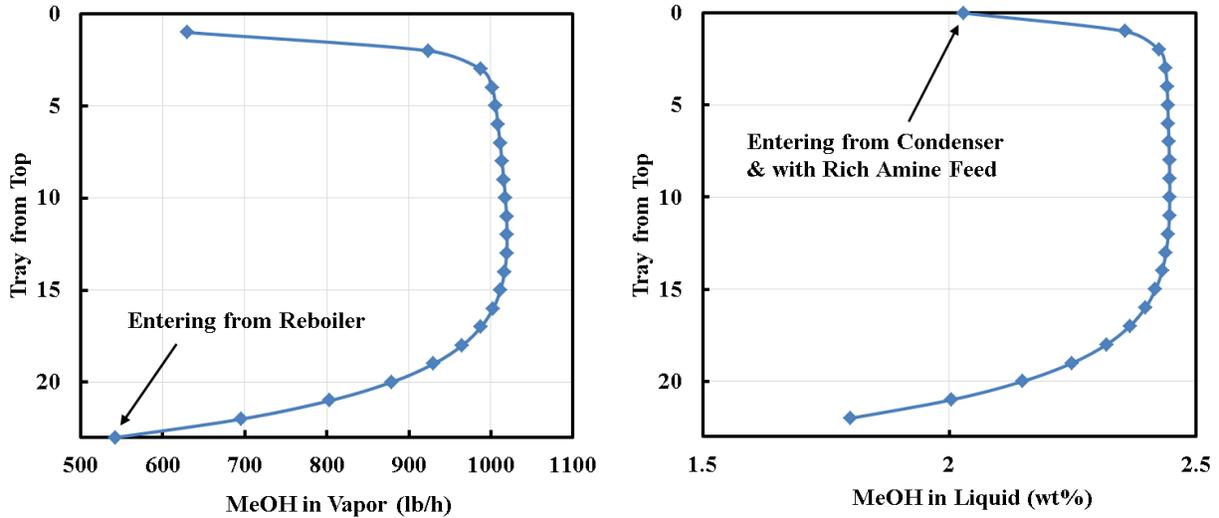
Flash gas make (via pressure reduction in the flash drum) can only remove 1% or less of the MeOH from the system so it is not really a significant outlet for methanol. Rather, it is a way to remove hydrocarbons from the amine before they enter the regenerator. Most of the methanol leaves with the gas from the regenerator; however, the lean amine recirculates a substantial flow of MeOH compared with the flow rate of MeOH entering the system with the raw feed. In other words, a substantial amount of methanol gets trapped in the recirculating amine flow. Using hot stripping gas in the flash drum may also offer a way to improve the quality of the treated NGL.

The concentration of methanol in the reflux water is quite high. Perhaps this offers an explanation for methanol trapping—the condensate from the overhead condenser returns a lot of methanol to the regenerator along with the condensed water. This makes it hard for methanol to get out of the system until it builds a substantial concentration in the regenerator, including in the rich amine to the regenerator. This returns methanol to the lean amine stream and prevents the treated NGL from achieving very low methanol levels. It should be noted with some interest that *high methanol levels in reflux water* may also afford the opportunity to remove methanol from the system via blowdown in just the same way ammonia is blown down in refinery amine systems.

METHANOL DISTRIBUTION IN THE REGENERATOR

Figures 2(a) and (b) show the simulated methanol distribution across the 22 trays in the regenerator in both the liquid and vapor phases. Each point refers to the stream leaving the tray. In the vapor phase, the mass flow rate of methanol is shown rather than its vapor phase concentration because the condensation of water causes concentrations to change which obscures what is actually happening. However, it can be seen that only near the bottom of the regenerator does MeOH strip from the solvent in a significant way. Equilibrium is reached fairly quickly as MeOH strips from the solvent over the last few bottom-most trays. Near the top of the regenerator the MeOH vapor flow and liquid concentration both drop again but now because of reabsorption of MeOH into the cooler solvent on and near the feed tray. In other situations involving much lower levels of MeOH in the stripper feed, we have predicted similar behavior in the streams flowing between the feed tray and the top of a regenerator, i.e., in the reflux section [3]. It should also be pointed out that the MeOH flow returned in the reflux is almost as large as its flow entering via in the main recirculating solvent stream. Reflux returns 99% of the methanol from the overhead vapor so the condenser is a serious trap for MeOH.

At the levels seen in the regenerator, methanol is well beyond the level of just a minor contaminant. It is possible that significantly high methanol levels in the treating solvent might drag additional hydrocarbons into the amine and, as a result, possibly contribute to foaming. Some research into this question could be valuable to the industry.



(a) Mass Flow Rate MeOH in Vapor

(b) Wt% MeOH in Liquid

Figure 2 Vapor and Liquid Distribution of MeOH in Regenerator

SUMMARY

Significant methanol removal from NGLs can be achieved by extraction into the lean amine used for CO₂ removal but it performs best with fairly high efficiency contacting. Methanol is hard to squeeze from the treating system because of its high affinity for water; however, mass transfer rate-based simulation is perfectly capable of predicting the performance of the CO₂ removal system, including the distribution of methanol everywhere in the unit.

Mass transfer rate-based simulation also reveals an interesting aspect of the methanol distribution in the regenerator—the regenerator struggles to remove absorbed methanol because the overhead condenser returns so much of it to the tower. This suggests that a possible way to remove more from the entering NGLs is to operate the condenser considerably hotter than in a conventional regenerator. In this way, less methanol might be recirculated back to the Contactor. Across the bottom seven or eight actual trays methanol is readily stripped. However, as vapor flows up the tower, equilibrium is soon reached. For this reason also, methanol removal in the regenerator is difficult and causes a rather high concentration in the recirculating solvent.

One way to remove a large fraction of methanol from the system is to blow down a substantial fraction of the reflux water. This stream is 16–17% MeOH and represents almost as high a flow of MeOH as the methanol entering with the rich amine feed itself. Returning it to the stripper rather than removing it from the system appears to be a terrible waste.

The presence of methanol in the regenerator even at these high levels is not expected to have a huge impact on the ability of the system to remove CO₂. The methanol, however, does affect the regenerator's hydraulic capacity because the vapor volume is 10% methanol, i.e., the vapor has a 10% higher flow rate than in the absence of methanol. Thus, tower capacity too can benefit from reflux blow down. The most important factor, however, is that high methanol in the regenerator negatively affects the ability of the system to remove methanol.

REFERENCES

- [1] Ng, H.-J., Schroeder H., *Vapor-Liquid Equilibrium Studies On Water-Methanol-MDEA-Hydrocarbon Systems*, RR-184, GPA, Tulsa, OK, April, 2003.
- [2] Courtial, X., Booneart, E., Valtz, A., Theveneau, P., Stringari, P., Coquelet, C., *Methanol Distribution (As a Contaminant) in Fractionation Products and Freeze Out Boundaries*, RR-219, GPA, Tulsa, OK, March, 2013
- [3] Govindarajan, Anand, Hatcher, Nathan A., Weiland, Ralph H., *Methanol Distribution in Amine Systems and Its Impact on Plant Performance*, Paper presented at the AIChE Spring 2015 meeting in Austin, TX, USA