CCR Technologies Inc.
Technical Bulletin
Clean Fuels Challenge

Strategic Considerations

In the Advance Program for the NPRA "Clean Fuels Challenge" 2001 conference, the question is posed, "What will refiners have to do to improve capacity, efficiency, and reliability of amine systems and sulfur units?". Here we will address the fundamentals of this question as it specifically relates to the amine unit itself, and how the amine unit relates to the sulfur plant.

Capacity

Generally the first issue considered in regards to capacity of amine units is the type of amine employed in the plant. Often amine strength expressed as weight percent is thought of as the capacity of the solvent, but this is not the case. The actual capacity of the amine employed in the plant needs to be expressed on a molar basis to see in actuality how potent each gallon of circulating solution is. Capacity for the various amines used in refining gas treating are listed below at the practiced maximum weight percents along with the corresponding molarity.

Amine	MEA	DGA®	DEA	MDEA
Maximum Weight Percent	18	50	25	45
Molarity (moles/liter)	3.0	4.8	2.4	3.8

Another consideration in regards to the capacity of the sulfur plant has been to employ MDEA in the amine unit to slip the maximum amount of CO_2 in the amine unit to preserve or increase the capacity of the sulfur plant. Unfortunately this has not proven effective in almost every application, and review of actual acid gas produced from all the amines shows little or no perceived benefit with employing MDEA.[1]

Efficiency

When efficiency is considered in the study of amine plants, energy consumption is generally the first topic that is reviewed. Often amine suppliers will try to sell one amine type over another due to energy savings due to reduced heats of reactions for a particular amine. Actual operating experience shows that energy consumption for the various amines are quite similar since the amine and water makes up a substantial portion of the regeneration heat requirements when compared to the dissolved acid gases.[1] The best way to improve efficiency and reduce energy consumption is to *circulate the minimum amount of gallons possible by maximizing the potency of each gallon circulated.*

Another item to be considered in regards to the efficiency of the amine plant is the ability to remove trace sulfur compounds. These items are becoming more important due to constraints on fuel gas quality and increased amounts of gas coming from conversion units (FCC and Coker). The efficiency of the various gas treating solutions in regards to trace sulfur removal is as follows.[1]

$$\underset{\text{Increasing Trace Sulfur Removal}}{\text{MDEA} < \text{DEA} < \text{MEA} < \text{DGA®} \longrightarrow}$$

Reliability

Reliability of the amine unit may be categorized into two areas. The first would be in regards to how the amine plant affects the reliability of the upstream sulfur plant, while the second would pertain directly to the reliability of the amine unit itself.

Hydrocarbon handling and solubility in the amine plant greatly affects the performance of the upstream sulfur plant. If hydrocarbons carryover from the amine plant to the sulfur plant, oxygen demand will increase and the potential exists to "soot up" the first converter bed. If the upset is large enough, the increase in pressure drop or a drop in bed conversion may bring the sulfur plant down for a catalyst change out. Therefore hydrocarbons need to be handled in the amine plant with proper flash drum size, design and operation. The flash drum is the best and only way to handle hydrocarbons in the amine since the vessel sees the whole flow of the stream and can effectively dispense the hydrocarbons continuously until the hydrocarbon ingress is brought under control.

It is also very important to make sure that hydrocarbon solubility is taken into consideration when evaluating the existing amine solvent, or when completing the evaluation of a possible amine conversion. Hydrocarbon solubility for the various amines employed in refining is listed here below.[2]

$$\text{MEA} =< \text{DEA} < \text{DGA®} < \text{MDEA} \xrightarrow[\text{Increasing Solubility of Hydrocarbons}]{}$$

When reliability of the amine plant itself is studied, corrosion and proper physical properties of the solvent are generally the two major items of importance. Corrosion has been described in the industry as the *single most expensive cost element* in amine plant operation, and physical properties can greatly affect ability to meet outlet gas specifications and affect amine consumption. Both of these issues may then be tied back directly to the solvent quality, or the level of contaminants and degradation products in the solution.

When solvent quality is considered, heat stable salts are the first item that comes to attention due to the recent focus in the industry due to their corrosive nature. However, HSS anions are not the only contaminants in amine solutions. There may be degradation compounds and contaminants, which can raise the corrosive potential of the solvent. Even with less corrosive degradation compounds present, unit reliability may be compromised. As the total level of degradation compounds and contaminants increase in the solution, and as the amine strength is kept at a constant level, the amount of water in solution drops. As the amount of water in solution drops the physical properties (surface tension, viscosity, etc.) will be adversely affected and may negatively impact the reliability of the amine plant. This is why the best way to improve (but not guarantee) the reliability of the amine plant is to have a proper plan in place to monitor and improve solvent quality when it falls outside of industry guidelines. It is important to understand that each amine type has specific degradation products generally present, and it is equally important to select a reclaiming technology that can remove **all** of the degradation products and contaminants present in the solution.

Summary

When dealing with the capacity, efficiency, and reliability of the amine plant and its effect on the upstream sulfur plant it is important to look at and understand the fundamentals of the amine solution. When the fundamentals are studied and understood, then the salesmanship or marketing of the amine supplier or service company cannot lead the plant owner in the wrong direction. When thinking of these fundaments, think of the following key points.

1. Capacity – Study on a molar basis
2. CO_2 Slip – Generally a false hope in refining systems
3. Energy Savings – Function of circulation rate, not amine type
4. Trace Sulfur Removal – Often over looked but becoming very important
5. Hydrocarbon Handling – Flash drum handles full flow effectively and continuously
6. Hydrocarbon Solubility – Understand where the solvents rank
7. Solvent Quality – Key for reliability, is solvent specific
8. Reclaiming – Not all technologies are created equal.

For more information contact CCR Technologies Inc. in Houston at 281-988-5800, or visit us at www.reclaim.com.

REFERENCES

1. Jenkins, J. L., “Use Amine Features To Guide Selection For Refinery Application”, Proceedings of the 1999 Sulfur Recovery Symposium.
2. Critchfield, J., P. Holub, H. Ng, A. E. Mather, F. Jou, and T. Bacon, “Solubility of Hydrocarbons in Aqueous Solutions of Gas Treating Amines”, Proceedings of the 2001 Laurance Reid Gas Conditioning Conference.