AdapT®

Why MDEA purity matters

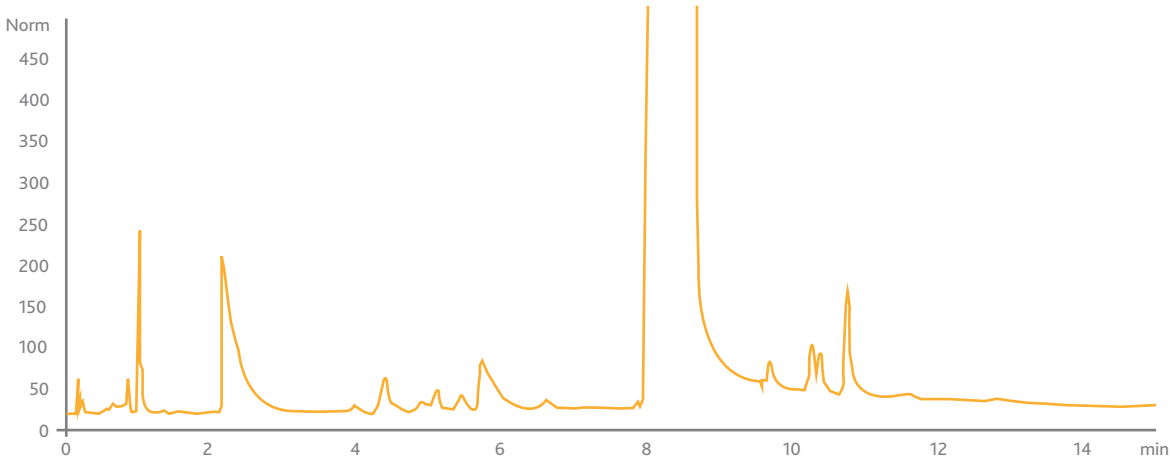
By Robin Matton, Application Development and Technical Services Manager

Introduction

MDEA (MethylDiEthanolAmine) is used frequently for selective removal of H_2S in both low pressure and high pressure gas treatment applications. Examples of applications that require selective sulfur removal are Claus tail gas treatment, acid gas enrichment and case-specific natural gas treatment. MDEA is a tertiary amine, which reacts quickly with H_2S but slowly with CO_2. This kinetic difference allows selective separation of H_2S from a gas stream. Please refer to Annex 1 for an overview of the chemistry. Primary and secondary amines, with exception of sterically hindered amines, possess no selectivity towards H_2S, because of their fast reaction with CO_2. However, primary and secondary amines may enter the MDEA either through degradation or the use of products with inferior quality. As will be illustrated in this paper, even small amounts of such non-tertiary amines can have a great impact on the selectivity and overall performance of the system.

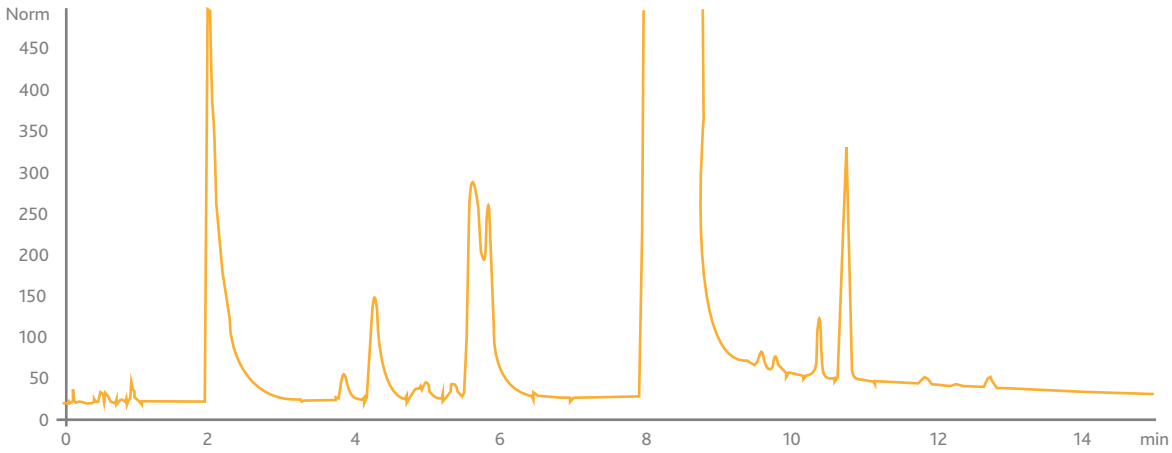
Sources of contamination

In the manufacturing process of MDEA, primary and secondary amines such as MMEA (MonoMethylEthanolAmine) or DEA (DiEthanolAmine) may be formed. Eastman's modern production installations are capable of achieving a consistent MDEA quality of over 99.8% with a maximum concentration of 1000 ppmw non-tertiary amines. However, MDEA from other sources may contain an elevated concentration of contaminants, as is illustrated by the below analytical results.

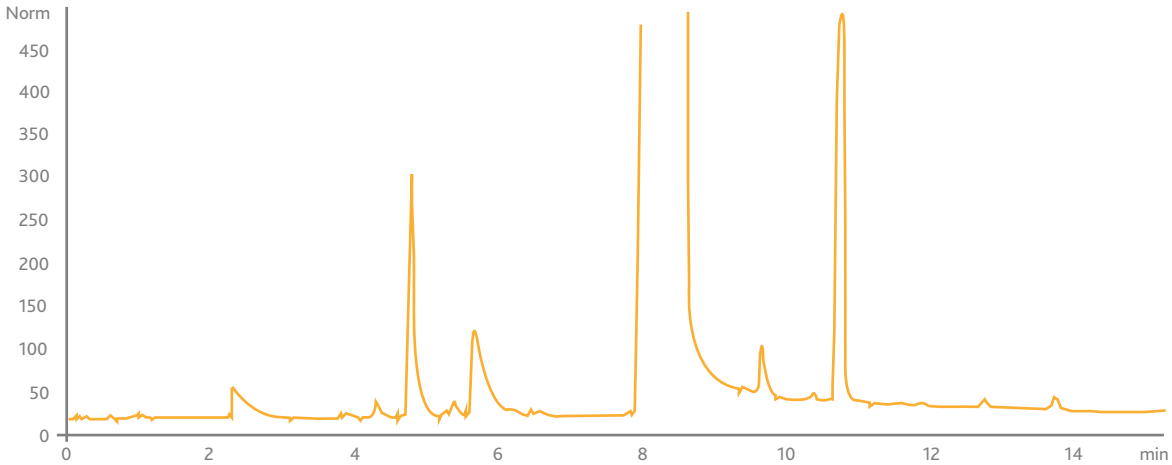


Graph 1

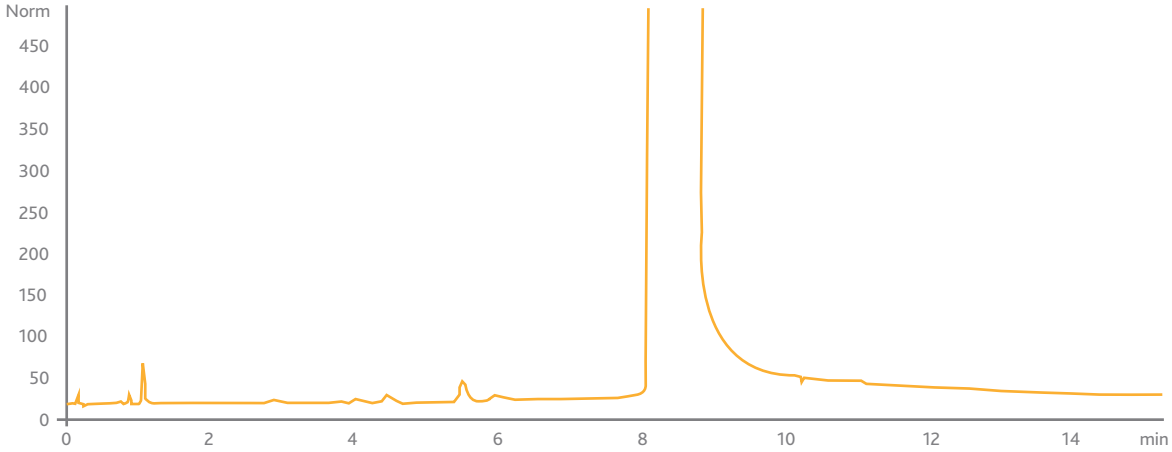
EASTMAN



Graph 2



Graph 3



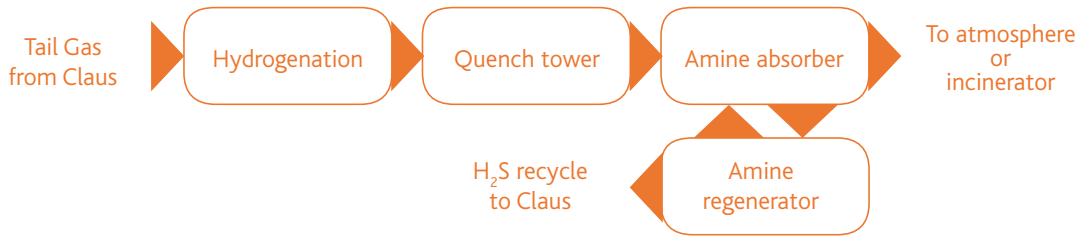
Graph 4

The above graphs contain gas chromatography results of MDEA from various sources. The first three are results of MDEA from other sources; the many peaks indicate a presence of significant quantities of nonionic impurities, such as DEA and MMEA. The fourth graph depicts the quality of Eastman MDEA; significantly less peaks and thus less impurities are present.

Another potential source of contamination with primary or secondary amines is degradation of MDEA within the gas treatment system. Although MDEA is generally recognized as a very stable amine in acid gas removal conditions, it is not completely resistant to chemical or thermal attack. Excessive regeneration temperatures can lead to increased thermal degradation. Oxidizing chemicals such as oxygen or sulfur-based acids are also known to attack the MDEA molecule, creating primary and secondary amines as well as other degradation products.

Case 1 – Claus tail gas treatment unit

The tail gas treatment process reduces sulfur vapor and SO_2 contained in the tail gas from the Claus process to H_2S, absorbs it in the absorbing solution (amine), and returns it to the Claus process, thereby achieving a high rate of sulfur recovery. Most TGT processes are comprised of a section where the sulfur content is reduced to H_2S, and a section where H_2S is absorbed by the amine resulting in high sulfur recovery rates. The treated gas from the amine unit contains between 10 and 250 ppmv of residual H_2S, which is dependent on the environmental legislation or general plant environmental targets, and is emitted to the atmosphere.



The tail gas contains significant quantities of CO_2 in addition to H_2S. Preferentially, only H_2S is recycled in the Claus unit, because CO_2 reduces the efficiency of the process and leads to the need for larger equipment. A selective amine such as MDEA is therefore preferred to remove the H_2S and slip CO_2 into the outlet stream, which is either vented or incinerated.

In order to study the impact of contamination by non-tertiary amines, a series of simulations were performed, varying the concentrations of MDEA and MMEA, a typical contaminant in such systems. See table to the right. The starting case is based on a 40 percent weight MDEA solution; below is the overall material balance.

The key operational parameters of the starting case are:

- Feed gas
  - Total: 803 kmol/h
  - H_2S: 15.3 kmol/h
  - CO_2: 91.9 kmol/h
- Solvent: 40 wt% MDEA, 0 wt% MMEA
- Lean solvent flow rate: 55 MT/h
- Reboiler energy input: 5.5 MW
- Lean solvent temperature: 40°C

	Tail Gas	Treated Tail Gas	Acid Gas
Temperature °C	40	40	45
Pressure Bar	1.6	1.4	1.5
Total Flow MMSCFD	16.1	15.7	0.4
Total Flow Nm^3/h	18,000	17,565	466
Total Flow kmol/h	803	784	21
Total Flow kg/h	22,887	22,178	730
Molecular Weight	28.5	28.3	35.1
Component mole %			
H_2O	4.68	4.84	6.51
H_2S	1.91	0.0046	72.48
CO_2	11.44	11.16	20.91
H_2	3.81	3.91	0.01
N_2	78.16	80.09	0.10

Next, an increasing amount of MMEA was added to the system, observing the impact on absorption of both H_2S and CO_2. The below table contains the key performance values for the system:

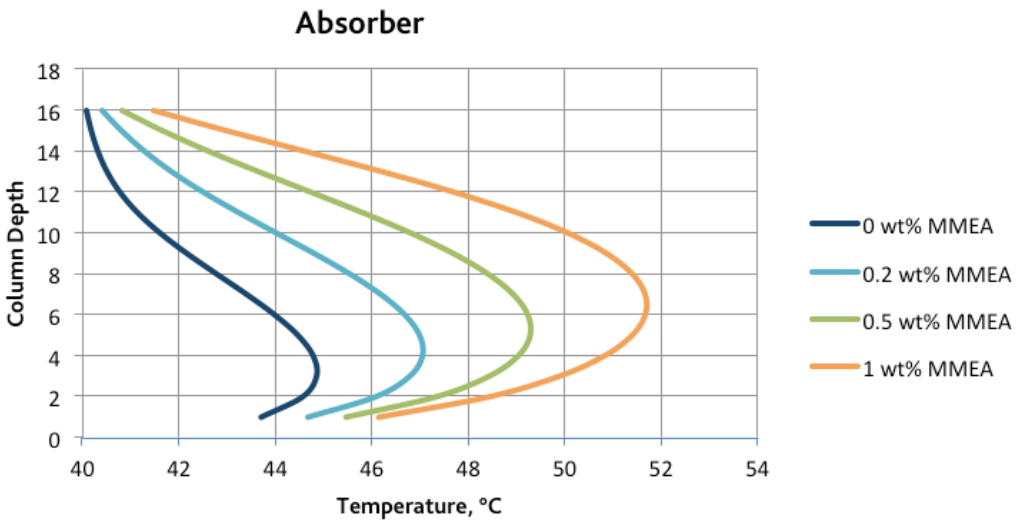
		Treated tail gas			Selectivity	CO_2 slip	Acid gas	
MDEA wt%	MMEA wt%	H_2S kmol/h	H_2S ppmv	CO_2 kmol/h			H_2S mol%	CO_2 mol%
40	0	0.04	46	87.5	20.8	95.2%	72.5	20.9
39.8	0.2	0.04	51	83.5	10.9	90.9%	60.5	33.2
39.5	0.5	0.07	87	80.1	7.8	87.2%	52.7	40.7
39	1	0.19	250	76.4	5.9	83.1%	46.6	47.5

Selectivity and CO_2 slip are key performance parameters to indicate how selective H_2S is removed from the tail gas stream.

Selectivity is defined as $$\frac{\frac{amount\ of\ H_2S\ removed}{amount\ of\ H_2S\ in\ feed\ gas}}{\frac{amount\ of\ CO_2\ removed}{amount\ of\ CO_2\ in\ feed\ gas}}$$

CO_2 Slip is defined as $$\frac{amount\ of\ CO_2\ not\ removed}{amount\ of\ CO_2\ in\ feed\ gas}$$

As can be seen from the above table, with as little as 0.2 wt% of MMEA in the solvent, there is an immediate, significant impact on the selectivity of the unit. At first, the increased amount of CO_2 mainly results in a lower quality acid gas, meaning that more CO_2 will be recycled to the Claus unit with negative effects on Claus unit size and efficiency. With increasing levels of MMEA, the H_2S removal itself starts to suffer, because CO_2 is replacing H_2S inside the rich solvent. The simulations conducted in this study predict a steep increase of the H_2S concentration in the treated gas from 46 to 250 ppmv. The effect of additional CO_2 absorption is also visible in the temperature profile inside the absorber. The increased temperature also negatively impacts the selectivity of the unit because it pushes the absorption equilibrium for H_2S in the wrong direction and increases the rate of absorption for CO_2.



Impact of selective formulation

A formulation designed for selective removal, such as Eastman AdapT 110, can improve the selectivity and overall performance beyond values typically achieved by unformulated MDEA. This is reflected in the data in the below table.

	Treated Tail Gas			Selectivity	CO_2 slip	Acid Gas	
	H_2S kmol/h	H_2S ppmv	CO_2 kmol/h			H_2S mol%	CO_2 mol%
MDEA	0.04	46	87.5	20.8	95.2%	72.5	20.9
AdapT 110	0.03	33	87.9	22.9	95.6%	74.4	19.1

Note that in this case, the performance was optimized toward high H_2S removal, rather than maximum selectivity, because of the relatively high selectivity of the starting case.

Case 2 – Natural gas treatment

Natural gas extracted from the earth may contain, in addition to valuable hydrocarbon components, undesirable contaminants such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S). Generally, strict specifications apply for H_2S removal for safety, corrosion and environmental reasons. For CO_2, however, the removal requirements vary strongly, as is illustrated in the below table:

Application	CO_2 Spec	H_2S Spec
Power Generation	5–20%	4–16 ppmv
Pipeline gas	2%	4–16 ppmv
LNG	50 ppmv	4 ppmv

Therefore, deep CO_2 removal is not always required. It can actually be cost-inefficient since it leads to a larger acid gas removal system and/or sulfur recovery unit and reduces the amount of gas that can be sold. Therefore it may be desired to selectively remove the sulfur, while minimizing pick-up of CO_2. Tertiary amines, such as MDEA are preferred. Contamination with primary or secondary amines is to be avoided.

In order to study the impact of contamination by non-tertiary amines, a series of simulations were performed for a natural gas treatment system, varying the concentrations of MDEA and MMEA. The starting case is based on a 35 weight% MDEA solution with the following targets

- CO_2 removal down to 2 mol%
- H_2S removal down to 4 ppmv
- H_2S concentration in acid gas > 40 wt% (dry) – suitable for Claus-type sulfur recovery unit

Below is the overall material balance:

	Feed gas	Treated gas	Acid gas
Temperature °C	35	43	45
Pressure bar	51.0	50.7	1.6
Total flow MMSCFD	96.8	93.3	3.8
Total flow Nm^3/h	108,098	104,116	4,243
Total flow kmol/h	4,823	4,645	189
Total flow kg/h	96,906	89,799	7,308
Molecular weight	20.1	19.3	38.6
Component mole %			
H_2O	0.14	0.21	6.05
H_2S	1.50	0.0004	38.12
CO_2	3.50	1.36	55.64
C1	80.89	83.93	0.16
C2	5.99	6.22	0.02
C3	3.00	3.11	0.01
C4	1.00	1.04	0.00
C5+	0.50	0.52	0.00
N_2	3.50	3.63	0.00

The key operational parameters of the starting case are:

- Absorber: 25 trays.
- Feed gas
  - Total: 4822 kmol/h
  - H_2S: 72.2 kmol/h
  - CO_2: 168.2 kmol/h
- Solvent: 35 wt% MDEA, 0 wt% MMEA
- Lean solvent flow rate: 100 m3/h
- Reboiler energy input: 9.1 MW
- Lean solvent temperature: 40°C

Next, an increasing amount of MMEA was added to the system, observing the impact on absorption of both H_2S and CO_2. The below table contains the key performance values for the system:

		Treated Tail Gas			Selectivity	CO_2 slip	Acid Gas	
MDEA wt%	MMEA wt%	H_2S kmol/h	H_2S ppmv	CO_2 kmol/h			H_2S mol%	CO_2 mol%
40	0	0.021	4	63	1.6	37.4%	38.1	55.6
39.8	0.2	0.024	5.1	61	1.6	36.2%	37.7	56.1
39.5	0.5	0.026	5.5	58.5	1.5	34.7%	37.2	56.6
39	1	0.029	6.3	55.2	1.5	32.7%	36.5	57.2

Again, presence of non-tertiary contaminants has an impact on selectivity and the overall performance of the system. However, the impact is clearly weaker in comparison with the tail gas treatment case. A key difference between both cases is the high pressure and the strict H_2S specification, requiring a relatively high solvent circulation rate which leads to a low overall selectivity. In cases where the operational conditions are close to the specification (e.g. for H_2S in treated gas or acid gas), the additional contamination may push the system beyond the limit, into malperformance.

Prevention and remediation

Once the non-tertiary amines have entered the system, it can be hard to remove them. Among the various techniques typically used for the reclaiming of MDEA-based solvents, such as ion exchange, electro dialysis and vacuum distillation, only vacuum distillation will actually remove these non-ionic contaminants.

As with most problems, prevention is preferred over remediation. Through procurement of solvents with higher purity and avoiding conditions that can degrade the solvent, build-up of contaminants can be slowed or stopped.

Conclusion

The purity of MDEA matters. In addition to possible degradation and associated corrosion effects, the selectivity towards H_2S removal can also be seriously impacted. In cases of low feed gas pressure, the effect is likely to be stronger; a few thousand ppm of contaminant can cause malperformance. It is important to consider the possible effects on treated gas composition, acid gas quality and downstream operations. Through procurement of solvents with higher purity and avoiding conditions that can degrade the solvent, build-up of contaminants can be slowed or stopped.

Annex 1 – Chemistry

All amines react in a similar fashion with H_2S. H_2S is transferred quickly into the liquid phase, where it forms bisulfide, protonating an amine in the process. These reactions are fast. This is illustrated in the below reaction scheme:

$$H_2S \rightarrow H^+ + HS^- \quad \text{(fast step)}$$

$$H^+ + R_3N \rightarrow H^+ + R_3NH^+ \quad \text{(fast step)}$$

Tertiary amines, such as MDEA form a bicarbonate with CO_2, which is slowly formed in the amine solution. This is illustrated in the below reaction scheme:

$$CO_2\ (gas) + H_2O \rightarrow H_2CO_3 \quad \text{(slow step)}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad \text{(slow step)}$$

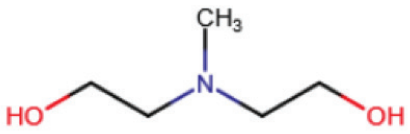
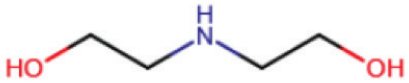
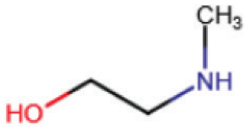
$$H^+ + R_3N \rightarrow R_3NH^+ \quad \text{(fast step)}$$

Non-tertiary amines can react must faster with CO_2 through the formation of a carbamate, because the amine group contains a hydrogen atom. The free proton formed in this reaction may protonate a second amine, which is also a fast step, but reduces the absorption capacity. This is illustrated in the below reaction scheme:

$$CO_2\ (gas) + R_2NH \rightarrow R_2NCOO^- H^+ \quad \text{(fast step)}$$

$$H^+ + R_2NH \rightarrow R_2NH_2^+ \quad \text{(fast step)}$$

Amine structures

MDEA:	*DEA:*	*MMEA:*
		

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