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ADVANTAGE OF METHYLDIETHANOLAMINE COMPARISON WITH OTHER AMINE IN REMOVAL FROM ACID GASES FROM NATURAL GAS COMPLEXES

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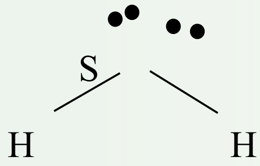
ABSTRACT

Year by years' number of world's population increasing, so grows the demand for energy. Natural gas is one of important energy resource. It uses not only generation power of energy, but need for produce chemical polymers for example polyethylene and polypropylenes. However, the presence of contaminants in the natural gas, such as H_2S and CO_2, is the cause of several operational and technical issues ranging from equipment corrosion, fouling, catalyst deactivation, and environmental pollution. Therefore, it is necessary to remove contaminants from these gaseous mixtures for their efficient and safe use in multiple applications. The objective of this review is to explore different methods the acid gas removal (AGR) processes. The choose correctly amine for AGR unit and the main parameters affecting the process have been discussed. In the first part of article, the chemical absorption processes are summarized, including the chemical mechanisms involved and a screening of the main amine-based solvents currently used in such processes. In the second part of article about conditions of chemicals and third part supported by experimental trends of process. Industrial applications of AGR processes have been included in the discussion. Finally, in this direct we indicate why MDEA is benefit choose for AGR system.

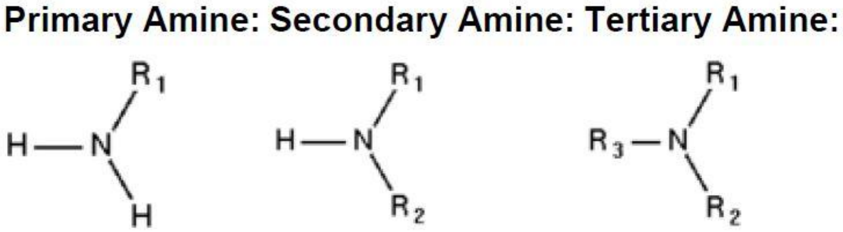
Keywords: Amine, acid gas, hydrogen sulfide, carbon dioxide, ucarsol, solvent, absorption, amine regeneration.

INTRODUCTION AND THEORY OF PROCESS.

Year after years rising prices for oil and petroleum products, the use of natural gas not only as a fuel but also for gas-chemical synthesis is becoming increasingly important. Natural gas undergoes several stages of purification and fractionation, one of which is the removal of acidic gases such as hydrogen sulfide and carbon dioxide[1]. Since hydrogen sulfide is a polar chemical molecule, its more active purification is therefore straightforward.



A wide range of sorbents can be used for its purification, from zeolites to various amines. Carbon dioxide can be a major challenge in acid gas purification. Since carbon dioxide is a non-polar molecule, it requires the correct selection of sorbent for its purification. Amine solutions are the most commonly used substances for this purpose. An amine is an organic compound that has a nitrogen containing functional group. Amines are classed as primary, secondary or tertiary depending on the number of organic constituent groups that are attached to it. Using the designation of “R” to represent such organic constituents, here are examples of amines:



They are also represented by written chemical formulas as shown for the following ones:

- Monoethanolamine (MEA): $OHCH_2CH_2NH_2$
-Diethanolamine (DEA): $(OHCH_2CH_2)_2NH$ -
-Methyldiethanolamine (MDEA): $(OHCH_2CH_2)_2NCH_3$

Amines are chemical solvents in that they react chemically with acid gases to remove them from a feed gas stream. The key acid gases removed by the AGFS process are H_2S and CO_2. We will discuss the mechanisms in the chemical reactions of acid gases with generic amines next. Although we will discuss only H2S removal, note that CO_2 will also undergo similar reactions[2].

Hydrogen Sulfide, H_2S or HSH, is a weak acid and ionizes in water to form hydrogen ions and sulfide ions:

$$HSH \rightleftharpoons H^+ + HS^-$$

Since it is a weak acid, only a small fraction of the HSH will ionize.

Ethanol amines are weak bases and ionize in water to form amine ions and hydroxyl ions:

$$(CH_2OHCH_2)_xNH_y + H_2O \rightleftharpoons (CH_2OHCH_2)_xNH^+_{y+1} + OH^-$$

where for MEA x = 1, y = 2, for DEA x = 2, y = 1 and MDEA x = 2, y = 0.

When H_2S dissolves into the solution containing the amine ions, it will react to form a weaklybonded salt of the acid and the base.

$$(CH_2OHCH_2)_xNH^+_{y+1} + HS^- \rightleftharpoons (CH_2OHCH_2)_xNH_{y+1}SH$$

The sulfide ion is thus absorbed by the amine solution.

This salt-formation reaction does not go to completion. As the arrows indicate, an equilibrium level of sulfide ion, HS-, remains in the hydrocarbon stream. The following equation summarizes the overall reaction:

$$(CH_2OHCH_2)_xNH_y + H_2S \rightleftharpoons (CH_2OHCH_2)_xNH^+_{y+1}SH^-$$

A similar reaction to equation (4) occurs with CO_2 that yields the amine salt and HCO_3^-.

Operating variables are adjusted to favor the forward reaction of equation (4) in the absorption step of the process, and, conversely, manipulated to favor the reverse reaction in the amine regeneration step of the process. The reversibility of this reaction permits solvent regeneration and continuous removal of H_2S and CO_2 by amine treating.

MDEA is a tertiary amine and a chemically selective solvent. MDEA has a strong chemical bond for H_2S and a weak chemical bond for CO_2. The acid gases (CO_2 and H_2S) react with the MDEA to form thermally regenerable salts. MDEA has a much lower vapor pressure than either MEA or DEA, so amine losses from vaporization are greatly reduced for MDEA systems treating gas streams.

The reaction between H_2S and MDEA occurs much faster than that of CO_2 and MDEA. The reaction between H_2S and MDEA is gas film diffusion-rate limited whereas the reaction between the MDEA and CO_2 is kinetically limited, therefore H_2S is preferentially favored. DOW's UCASOL formulated solvents, are MDEA-based solvents which take advantage of this difference in CO_2 and H_2S absorption to enable varying degrees of selective acid gas removal[3].

The reactions presented above are exothermic. A temperature rise is expected for the feed gas, as it is processed in the absorber, which generally approaches the lean solvent temperature as it travels up through the column. The solvent temperature, however, can either increase or decrease through the absorber depending on how much heat is transferred to the feed gas. A solvent temperature rise can be expected with higher feed gas temperatures and/or higher gas/liquid ratios, since more heat is transferred from hotter feed gas or generated by the heat of reaction at low gas/liquid ratios. This adsorption mechanism is shown below.

During the intimate mixing, acid gas transfers from the natural gas feed to the UCARSOL solvent. In a perfect or theoretical stage of contact, dynamic equilibrium would be reached. At conditions of dynamic equilibrium, there is no further net transfer of acid gas from the natural gas feed to the solvent; that is, the rate of acid gas transfer from the hydrocarbon to the UCARSOL solvent equals the rate of acid gas transfer from the UCARSOL solvent back into the natural gas feed. In any real or actual stage of contact, true or complete equilibrium is not reached. The closer the approach to true equilibrium, the more efficient is the stage of contact.

The concept of the countercurrent principle is that as the natural gas feed proceeds upward stage by stage, it will be in contact with UCARSOL that contains less and less acid gas (or that is leaner and leaner). Therefore, at the last stage of contact, the "cleanest" natural gas feed will be in contact with the leanest UCARSOL solvent. Conversely, at the first stage of contact, the "dirtiest" natural gas feed will be in contact with the richest UCARSOL solvent. This type of arrangement results in an approach to equilibrium favorable to the least possible amount of acid gas in the natural gas feed leaving the top of the absorber.

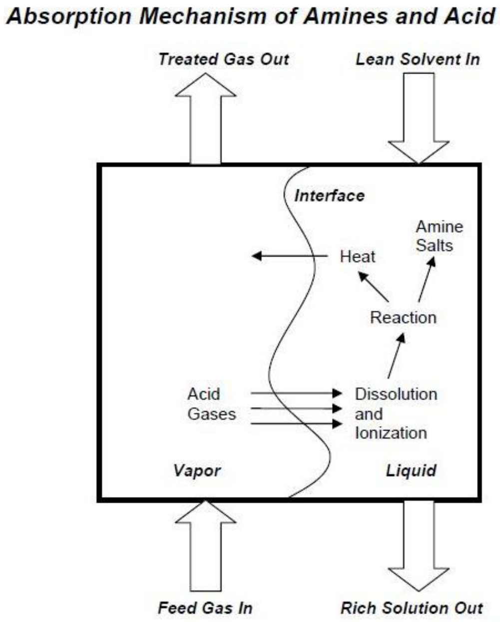


Figure 1

Absorption scheme amines

EXPERIMENTAL

CHEMICALS AND MATERIALS

Ucarsol solvent loadings

The acid gas loading of an amine solvent is defined as follows:

$$\text{Acid gas loading} = \frac{\text{Mole of acid gas}}{\text{Mole of UCARSOL}}$$

It should be noted that the denominator of the equation is specific to only the moles of UCARSOL and not moles of UCARSOL solution.

To achieve low H_2S and CO_2 (acid gas) levels in the treated gas in the absorber, it is necessary to strip the residual levels of these components in the entering rich amine stream to very low loadings (typical loading is <0.015 mole acid gas/mole UCARSOL). Steam stripping occurs in the regenerator at high temperatures and reverses the reactions presented above. The steam reduces the partial pressure of H_2S and CO_2 over the amine, thus reducing the equilibrium concentration (or loading) of these components in the UCARSOL solvent. Steam for stripping is generated in the reboiler that use medium to low pressure steam or hot oil to vaporize a portion of the water from the UCASOL solvent[5].

Solvent losses

As long as there are no contaminants in the feed gas and makeup water, there should be no degradation of the UCARSOL solvent in an AGFS unit typically no reclaimer is required. However, a quantity of normal solvent losses can occur in the course of normal operations as listed below:

1. Trace amounts of solvent are present in the purge water
2. Trace amounts in the outlet gas streams from

1) Absorber overhead treated gas
2) Reflux Drum overhead acid gas

Description of flow with controls

In Amine Guard FS units, the natural gas feed enters the bottom of the Amine Absorber, and is counter-currently contacted with lean UCARSOL solvent.

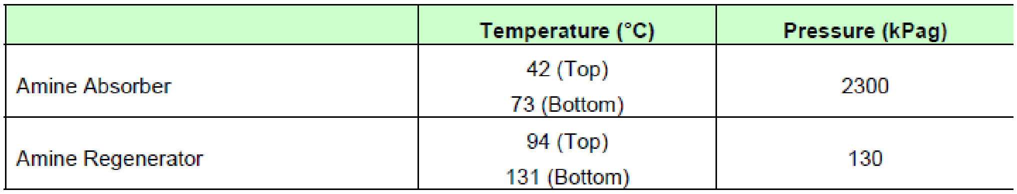
The UCARSOL solvent absorbs H_2S and CO_2. The treated gas passes to the Amine Absorber, water wash section to remove entrained solvent before passing through a mist eliminator and leaving the system.

The rich amine solvent leaves the bottom of the Amine Absorber, and is routed to Amine Regenerator.

The flashed rich solvent tangentially enters the Amine Regenerator, and is completely stripped of acid gas by rising steam vapors generated by the Amine Reboiler. The lean solvent exits the Amine Regenerator, and is recirculated to the Amine Absorber.

The acid gas is contacted with reflux water over the reflux water wash trays in Amine Regenerator, to remove any entrained solvent. The acid gas is cooled and separated from the condensed water in a Regenerator Reflux Drum. The condensed water is returned to the Amine Regenerator top as reflux water and acid gas vent to atmosphere.

The operating conditions of main equipment are as follows;



	Temperature (°C)	Pressure (kPag)
Amine Absorber	42 (Top) 73 (Bottom)	2300
Amine Regenerator	94 (Top) 131 (Bottom)	130

Table 1 operating conditions of solvent

Lean solvent conditions

1. Temperature

The absorption of H_2S and CO_2 in the UCARSOL solvent is enhanced at lower operating temperatures. Consequently, units are typically designed for the minimum lean solvent temperature attainable within the cooling medium available.

However, there are other limitations to how low the lean solvent temperature can be targeted. In some case, too low a solvent temperature can condense hydrocarbons in the feed and cause a hydrocarbon buildup in the Amine Absorber.

Specified lean solvent temperatures typically range from 27 ºC to 49 ºC and can vary based on feed conditions and cooling medium availability. The lean solvent temperature should be kept at least 2.5 ~ 5 ºC (5 ~ 10 ºF) above the feed temperature to avoid the condensing of hydrocarbons. Each AGFS unit is designed for a specific solvent circulation rate at a specific lean solvent temperature. Therefore, under normal operating conditions, the lean solvent temperature should be maintained at the design value specified for that particular unit.

2. Circulation Rate

The required solvent circulation rate for a given unit is dependent on many factors:

- Lean Solvent Temperature
- Lean Loading (moles acid gas/moles UCARSOL)
- Feed Gas Conditions
- Product Specification
- Absorber Internals (packing or trays)

The specified solvent circulation rate is one of the many conditions of the lean solvent that must be maintained in order to meet the desired product specification.

3. Concentration

The concentration of uncombined amine ions is favored by high amine concentration in the amine solution, good regeneration, and freedom from strong acids. Practical and economical considerations confirmed by field experience have generally shown that the optimum amine concentration is between 15 to 50 wt% for amines in general depending on the amine. This is based on the lowest heat requirement for the desired H_2S and CO_2 removal, the lowest chemical losses, and the fewest operational problems[6].

The free amine ion concentration in the lean amine is mainly affected by the efficiency and control of amine regeneration. The fewer sulfide and carbamate ions there are in the lean amine, the greater is the free amine ion concentration available for removal of H_2S and CO_2.

In this project, the recommended concentration for the UCARSOL is 45 wt%. The specified solvent concentration must be maintained in order to ensure the unit meets product specifications.

In order to achieve low H_2S and CO_2 (acid gas) levels in the treated gas in the Absorber, it is necessary to strip the residual levels of these components in the entering lean amine stream to very low loadings (typical loading <0.01).

A variable that affects acid gas loadings is the steam stripping duty. Steam stripping occurs in the Amine Regenerator at high temperatures and reverses the reactions presented above.

The steam reduces the partial pressure of H_2S and CO_2 over the amine, thus reducing the equilibrium concentration (or loading) of these components in the UCARSOL solvent. Steam for stripping is generated in a Amine Reboiler, which uses heat provide by low pressure steam to vaporize a portion of the water from the UCARSOL solvent.

This reduction of acid gas in the solvent is what increases the driving force for removing the acid gas from the feed gas.

The acid gas loading in the lean solvent can be maintained with the proper operation of the regeneration section of the unit. The process variables that directly affect the lean loading can be maintained to ensure adequate stripping of the acid gas is achieved.

RESULTS

Below is the temperatures trend in the amine regenerator with DEA and MDEA

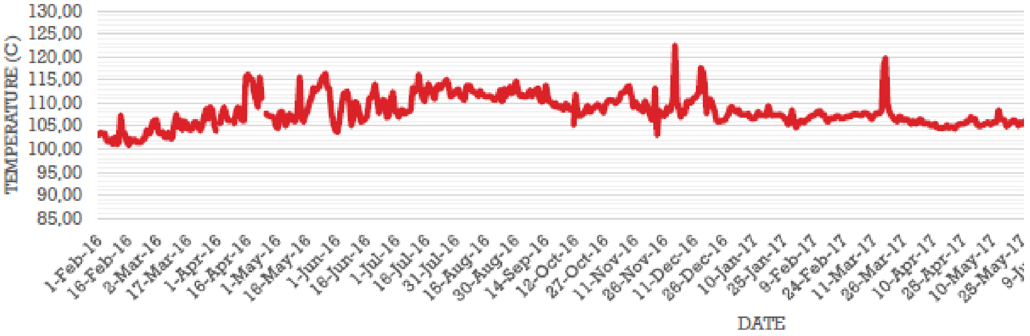


Figure 2 trends bottom temperatures amine regenerator with MDEA

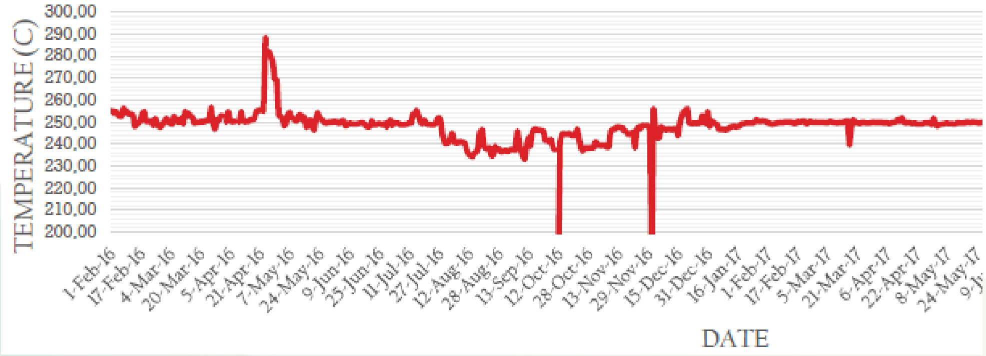


Figure 3 trends bottom temperatures amine regenerator with DEA

In this we can see, DEA requires twice as much energy to regenerate compared to MDEA. This is because DEA forms a more stable salt than MDEA. Therefore, when choosing an amine, MDEA is a better choice because it requires less energy to regenerate and has a longer circulation life.

CONCLUSION

In a conclusion we must say correctly choose acid removal system and reactant is more important for other gas chemical process. Decreasing percentage acid gas has a beneficial effect to cracking process and decreasing quantity base in neutralization after cracking. Using MDEA and amine removal system more benefit because this solvent more active and required less temperature than other amines.

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