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Carbon Capture Using Amine-Based Technology

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Summary

Amine based solvents have been used in the oil and gas industry for some sixty plus years to remove CO_2 from gas streams. This technology can be used for carbon capture from pre or post combustion gasses in power plants as well. Certain challenges will arise however, due to the unique composition of flue gasses as well as the low pressures associated.

In this paper we discuss how to utilize as much existing and proven technology as possible for effective carbon capture, as well as the subtle but important differences between historical amine systems and the future.

This paper will cover the general purpose and flow scheme of a carbon capture amine plant, some brief comments on operating conditions, as well as an overview of the challenging areas of oxygen reacting with amine, low pressure CO_2 removal, and energy consumption.

Amine Applications

Amines are currently used to remove CO_2 from gas streams in several areas of the oil and gas industry, and have been for over sixty years. In refining, amines are primarily used to remove H_2S from hydrocarbon gas (and liquid) streams from several various sources. Although CO_2 may be present, it is not normally a high priority as it is virtually useless to the refinery. The amine system will pick most if not all of the CO_2 out of the gas, and it eventually goes to incineration. Refineries often have problems related to heat stable salts, which is where stronger acids than H_2S or CO_2 are present and they form a very strong bond with the amine.

Amines are also used around the world in natural gas processing plants to remove H_2S and/or CO_2. The level of acid gas removal depends on the "sales gas specification", but on average the treated gas cannot exceed 2 mol% CO_2. The gas streams being treated in these plants range greatly in pressure and composition, and for this reason many different types of amines are utilized depending on the situation. Gas plants have historically had difficulty in the area of oxygen entering the amine system and causing solution degradation.

Tail gas treating is done in both gas plants and refineries, as an option to further reduce the H_2S content of the gas exiting a sulphur plant. The primary focus of a tail gas treating plant is to selectively remove H_2S from the gas, while leaving CO_2 in. This is done at extremely low pressures, which makes acid gas removal from the gas very difficult.

Utilizing amines in the carbon capture industry is certainly possible, though not without unique difficulties. Although no single one problem is unique, the combination of them is. Carbon capture involves removing CO_2 from a very low pressure gas stream, which contains high levels of oxygen. The most proven type of amine for CO_2 removal at low pressure, monoethanolamine, unfortunately will partially degrade when reacted with CO_2. Carbon capture takes the main problems from each individual application of amine: refining, gas plants, and tail gas; and combines them. Heat stable salt formation, chemical degradation, and low pressure treating are a day-to-day battle in the carbon capture process when using amines.

Amine Technology

Amines, having a pH of approximately 10, are medium strength bases which are used to remove CO_2 from gas streams. The CO_2, in the presence of water, is acidic, which then reacts with the amine to form a salt. Amine that has been reacted with CO_2 is known as "rich amine". The reaction between primary or secondary amines and CO_2 is almost immediate.

The gas and amine contact each other in an absorber tower, which is typically filled with random or structured packing and is several meters in height. Gas enters at the bottom of the tower and amine at the top. The two flow counter-currently, with CO_2 being steadily transferred from the gas into the liquid. By the time the gas reaches the top of the tower, it lastly contacts the fresh "lean" amine. The amount of CO_2 in the gas will be in equilibrium with the CO2 in the amine; the less CO_2 in the amine, the more readily CO_2 will transfer out of the gas.

The gas exiting the absorber, known as "treated gas", will be composed of mainly hydrogen and water and can be vented to atmosphere or incinerated.

The CO_2-loaded rich amine is heated in a lean/rich heat exchanger before entering the regenerator tower. The purpose of the regenerator is to reverse the bond between the amine and CO_2. The reaction is reversed by adding heat to the amine as it travels downward though the tower. Heat is supplied in the form of steam, which is generated at the bottom of the tower in the reboiler.

The reboiler is the largest consumer of energy in the amine plant, and therefore a main focus of plant optimization studies. The reboiler is powered by a heat medium, often low pressure steam, but can also be hot oil, glycol, or even direct fired. Inside the reboiler, the water portion of the amine solution boils and produces steam. The steam then rises though the regenerator tower, supplying heat for the endothermic reaction which breaks apart the bond between the amine and CO_2.

The steam generated in the reboiler has three main purposes:

- sensible heat - to increase the temperature of the amine to the boiling point,
- reaction heat – to reverse the bond between amine and CO_2
- reflux heat – steam must be exiting the top of the regenerator in order to sweep the now-liberated CO_2 out of the tower, and also to provide a source of reflux flow for the system.

The regenerated amine leaves the reboiler and is cooled first in the lean/rich exchanger, and further cooled in the amine cooler. It is filtered, and ready for re-injection into the absorber.

The gas stream leaving the regenerator is almost pure CO_2. It can be liquefied and sold, or compressed and pumped underground for long-term/permanent storage or sequestration.

Reaction Chemistry

The reactions of CO_2 in the gas phase with as aqueous amine solution commences with the physical dissolution of CO_2 into the water phase. The CO_2 molecule has to be transferred from the gas phase to the liquid phase for any meaningful reaction to occur. Some interfacial reactions are possible, but for the most part reactions are in the liquid phase. From that point on, there are two main reaction pathways for CO_2 reaction with amine molecules. These are:

1) Acid-Base Reactions. The amine acts as a base to react with carbonic acid, a product of the reaction of water and CO_2
2) Nucleophilic Reactions. The amine reacts directly with dissolved CO_2 molecules. Subsequent reactions take place but the initial step is an SN_2 reaction

Acid-base reactions tend to be extremely fast as opposed to nucleophilic reactions that are usually diffusion controlled however in CO_2 removal the acid base pathway is slow because the fist the slow generating carbonic acid need to be generated. The first event to take place in a CO_2 reaction with amine is the transfer of CO_2 from the gas phase to the liquid phase. Then the CO_2 molecule suffers hydrolysis to produce carbonic acid and bicarbonate.

CO_2 (gas) $\longleftrightarrow$ **CO_2** (physical reaction of CO_2 dissolving in water)
$CO_2 + H_2O \longleftrightarrow$ **H_2CO_3** (chemical reaction of CO_2 and water to produce carbonic acid)
$H_2CO_3 \longleftrightarrow$ **HCO_3^{-1}** $+ H^{+1}$ (chemical dissociation of carbonic acid to form bicarbonate)

<u>Nucleophilic Pathway</u>

This reaction mode involves the direct attack of the amine into the central carbon of CO_2. The intermediate then suffers an internal H^{+1} transfer to produce a carbamic acid. This further react with the amine to form the ammonium salt. In the case of a tertiary amine this is not possible (no H), hence there is no reaction. It is important to indicate that the reaction is slower and less efficient as the amine goes from a primary to a secondary amine. This is because the R groups physically block the amine N atom from reaching the CO_2.

Reactions with Primary and Secondary Amines (for example MEA and DEA)
$R_1R_2NH +$ **CO_2** $\longleftrightarrow R_1R_2NH\text{-}COO$ (nucleophilic reaction of amine with CO_2 forming an internal salt)
$R_1R_2NH\text{-}COO \longleftrightarrow R_1R_2N\text{-}COOH$ (internal H^{+1} transfer forming a carbanic acid)
$R_1R_2N\text{-}COOH + R_1R_2NH \longleftrightarrow R_1R_2N\text{-}COO^{-1} + R_1R_2NH_2^{+1}$ (ammonium carbamate salt)

Reaction with Tertiary Amines (MDEA)
$R_1R_2NR_3 +$ **CO_2** $\longleftrightarrow R_1R_2NR_3\text{-}COO$ (nucleophilic reaction to generate an internal salt)
$R_1R_2NR_3\text{-}COO \not\longleftrightarrow R_1R_2NH\text{-}COOR_3$ (no reaction, R transfer is not possible)
$R_1R_2NH\text{-}COO \longleftrightarrow R_1R_2NH +$ **CO_2** (reaction reversal back to products. Essentially no reaction)

Even though a salt is the product of the acid-base reaction, the product is instantaneously dissolved in the water solvent forming a collection of ions (positive ions are called cations and negative ions are called anions). These ions are highly hydrated with a layer of water molecules making them very stable and avoiding reaction reversal under normal conditions. These reactions however, can be reversed if exposed to the correct conditions in terms of pressure and temperature; this is exactly what takes place in the regenerator.

Acid-Base Pathway (primary, secondary and tertiary amines)
A different pathway is the acid-base reaction. This reaction takes place not with CO_2 directly but with the product if the reaction of CO_2 with water (carbonic acid). This reaction is fast and it is basically independent of the alkanol R substituents in an amine. Some amines will have faster reaction rates depending on inductive effect of the substituents. Acid-base reactivity is slightly faster with tertiary amines, followed by secondary and primary amines.

$R_1R_2NH + \mathbf{H_2CO_3} \longleftrightarrow R_1R_2NH_2^{+1} + HCO_3^{-1}$ (ammonium bicarbonate)

Both of these reactions mechanisms (acid-base and nucleophilic) represent how CO_2 is removed from a stream using an amine solutions. One of the most suitable amines for CO_2 removal from a gas stream is MEA. This particular molecule is the most reactive via a nucleophic pathway (the N atom is highly exposed to react) and also has good acid-base reactivity. As far as process condition and in order to satisfy both reaction mechanisms outline above, a temperature of 43 - 46 ^oC has been shown to be the most effective.

Types of Amine
There are several different types of alkanolamines on the market, all of which will remove CO_2 from gas streams to one degree or another. Given the unique properties of post-combustion gas from a power plant however, only a couple of amines are applicable to this process.

Monoethanolamine (MEA), a primary amine, is the most proven and reliable CO_2 removal agent on the market. It is readily available, and the lowest price of all the different types of amine. MEA has several advantages as well as disadvantages.

Advantages of MEA:

1. Strongest amine. MEA is more reactive than any other type of amine and therefore forms the strongest bond with CO_2. It is very reliable, and will endure higher levels of contamination or improper operating conditions yet still remove CO_2 compared to other amines.
2. Low molecular weight. MEA is not a complicated molecule, and the molecular weight of 61 is the lowest of any amine. Because of this, even a low strength MEA solution is very potent. Running MEA at low strengths but still being able to remove CO_2 is advantageous in that it minimizes the risk of corrosion due to degraded MEA and heat stable salts.
3. Price and availability. MEA is the least expensive as well as most readily available of all amines.

4. Online reclaiming. MEA can be reclaimed at atmospheric pressure, something which cannot be said for secondary or tertiary amines. Atmospheric reclaiming is used to remove degradation products and heat stable salts which would otherwise build up in the solution, increasing the corrosive tendency and reducing the strength of the bond between amine and CO_2.

Disadvantages of MEA:

1. High heat of reaction. Although the strong bond between MEA and CO_2 is an advantage in the absorber, it is a disadvantage in the regenerator as it requires quite a large amount of energy to break the MEA:CO_2 bond. More so than any other type of amine.
2. Degrades in the presence of CO_2 and oxygen. Both of these components are present in post combustion gas, so special equipment is needed to keep the degradation products from building to corrosive levels.

Another type of amine which would work in post-combustion gas CO_2 capture is "promoted" MDEA. MDEA is a tertiary amine, which, ironically, has historically been used in situations where CO_2 removal is NOT desired. MDEA itself does not react directly with the CO_2 molecule. With the addition of a promoter however (most commonly piperazine), MDEA has the ability to remove CO_2, but without the two disadvantages of MEA; degradation and high heat of reaction.

Advantages of promoted MDEA:

1. Lower heat of reaction compared to MEA, therefore less energy intensive
2. Does not degrade in the presence of CO_2

Disadvantages of promoted MDEA:

1. Still degrades in the presence of oxygen, and will form corrosive heat stable salts as well
2. Online reclaiming to remove oxygen degradation and corrosion products not possible
3. Very expensive and in lower supply compared to MEA

Challenges of carbon capture

Although theoretically possible, utilizing amines to remove CO_2 from the post combustion gas created in coal fired power plants is challenging for several reasons:

1. Low pressure gas increases difficulty of transferring CO_2 from the gas into amine
2. Oxygen content of the gas can cause amine degradation and acid formation
3. CO2 degradation of primary (and secondary) amines
4. High energy consumption
5. Very large facilities
6. Finding a suitable location for the removed CO_2

Comments on each challenge:

Low pressure of absorber: because partial pressure is the "driving force" to transfer CO_2 from the gas phase into the liquid phase, successfully achieving this under low pressure conditions can be difficult, though it depends somewhat on the target level of CO2 in the treated gas. Deeper levels of CO_2 removal require lower CO_2 loaded lean amine. This can only be accomplished by increasing the energy duty of the reboiler.

Degradation: The oxygen content of the inlet gas will react with the amine and form degradation products and heat stable salts. All amines degrade in the presence of oxygen unfortunately. CO_2 also causes degradation, but only in primary and secondary amines (MEA and DEA). The degradation products and heat stable salts can increase the viscosity of the amine (requiring more energy to heat and cool) and possibly increase the corrosiveness of the solution. Furthermore, degraded amine is not "amine" anymore and not useful in removing CO_2. Managing degradation is typically a combination of these techniques:

- Prevention
- Reclamation
- Purge and replace amine

Prevention

The prevention or minimization of degradation (by either O_2 or CO_2) is mainly done by keeping the temperature of the absorber to a minimum. When CO2 reacts with amine, it is exothermic, meaning heat is generated. In order to quench the temperature, interstage coolers are used, whereby the amine is taken out of the middle of the absorber, cooled, and re-injected. There can be more than one cooler depending on the height of the tower.

Reclaimers

Thermal reclaimers are used on MEA systems to remove degradation products and heat stable salts. The reclaimer looks much like the reboiler, but runs at a higher temperature. The amine and water are vapourized and returned to the regenerator, but the higher boiling point degradation products remain behind. When the reclaimer is full of degradation products, it is dumped, cleaned, and put back online. Normally 1-3% of the circulation solution is reclaimed.

Heat stable salts can also be removed in the reclaimer if caustic is added to the amine solution beforehand. The strong caustic replaces the amine in the HSAS molecule, thus freeing the amine and "neutralizing" the salt. The salt does not boil and is therefore removed in the reclaimer.

MDEA cannot be reclaimed at atmospheric pressure, because the boiling point of the amine and the degradation products are too close to the same.

Purging and replacing amine

This is an "easy" fix to the build up of degradation and heat stable salt products, but should only be done as a last resort. There is cost associated not only with the purchase of fresh amine, but also with the disposal of the current. With proper temperature control of the absorber and operation of the reclaimer, purging amine should not be necessary.

<u>High energy consumption</u>

Energy is consumed in amine systems primarily by the reboiler, because heat is necessary to reverse the reaction between amine and acid gas. Along with reaction heat, the reboiler is also required to produce sensible heat as well as reflux heat (which is the left over steam used to sweep the CO_2 out of the regenerator).

The sensible heat duty [Q=m*c*(T2-T1)] is the single largest component out of the three. Sensible heat can be kept to a minimum by optimizing "m", the mass or circulation rate of amine, and the temperature difference between when the amine enters the regenerator and inside the reboiler. This is the function of the lean/rich exchanger.

Amine circulation rate can be minimized by operating the MEA at a high strength of 30% (with a reclaimer online to control degradation products) and a molar rich loading of 0.4 moles of CO_2 per mole of MEA.

<u>Size of the amine facility</u>

Compared to standard gas plants or refineries, carbon capture facilities are much much larger. This is because of the large volume of gas which must be processed as well as the low pressure of the gas.

Papers published on the design of carbon capture amine plants list some key design details which can reduce the cost of the amine plant construction:

- The inlet gas does not need to be cooled. In typical amine operation, the amine temperature is maintained at approximately 10 C warmer than the inlet gas. This is to prevent the condensation of hydrocarbons
- Utilizing structured packing has been shown to result in the highest gas capacity for a given area. Therefore if structured packing is specified in the design, the absorber will be a smaller size compared to random packing.
- Utilize plate and frame exchangers instead of shell and tube.
- To minimize energy to the reboiler, the lean amine can be "flashed" in a separation vessel, whereby the steam and heat being flashed is returned to the regenerator. This may reduce reboiler duty by up to 30%.

<u>Captured CO_2</u>

The final challenge in this process, is that once the CO_2 has been removed from the gas, what to do with it? In some areas, there is a market for CO_2 as a miscible flood in oilfields. The CO_2 is injected downhole and helps loosen the oil, making it flow easier. This is known as CO_2 flooding, and there are several successful case studies.

If no oilfields are in the vicinity of the power plant however, then the CO_2 must be sequestered underground. Large underground caverns are used, but the CO_2 may have to be piped long distances.

Conclusion

Removing CO_2 from gas streams using MEA or activated MDEA is a proven, tried-and-true technique. For the most part, existing technology could be used for this application, with perhaps the addition of interstage coolers on the absorber.

None of the individual challenges facing carbon capture are unique to the amine industry, however the combination of challenges is. Very large facilities, low pressure treating, combined with oxygen and CO_2 degradation plus the added problem of what to do with the captured CO_2 has not been done in any wide-spread way. The technology and know-how exists to handle all of these problems however, and with proper operation to minimize energy consumption amine based technology provides effective, long-term CO_2 removal from post-combustion gas streams.