How DEA Affects CO$_2$ Removal by Hot Pot

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In ammonia production, CO$_2$ removal from synthesis gas is an important processing operation. There are a number of technologies for taking raw syngas from 17% CO$_2$ to a few 100s of ppmv. This article focuses on CO$_2$ removal by a two-stage Benfield process, probably the most commonly-seen carbonate-based technology.

Carbonate processes are characterized by absorbers and regenerators both running very hot (typically ranging from 100 – 130°C) so that heat integration in the form of large lean-rich cross exchangers is unnecessary. Regeneration is forced by a pressure swing from a high absorber pressure to a low regenerator pressure, aided by steam stripping, as opposed to the temperature swing and predominantly steam stripping on which amine absorption systems rely. Nevertheless, removing CO$_2$ is still energy intensive, and a variety of conservation schemes are used.

High temperatures in CO$_2$ service make for a very corrosive environment. To avoid the use of corrosion inhibitors, vessels are sometimes stainless clad with stainless process piping. Characteristically, the absorber and regenerator tend to be very tall (50 – 60 m overall) holding five or six beds of random packing, each between 5 and 8-m deep.

Process Chemistry

Aqueous potassium carbonate and bicarbonate are in the form exclusively of K^+, HCO_3^- and $CO_3^=$ ions. When CO$_2$ dissolves into water it forms carbonate and bicarbonate ions, and very little is present as molecular CO$_2$. Hot potassium carbonate solutions are an ionic soup and the notion that these ions are associated with each other in the form, for example, of K_2CO_3 is fictitious. Carbon dioxide hydrolyses in solution with the hydroxide ion from dissociated water:

$$H_2O \rightleftharpoons H^+ + OH^- \tag{1}$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \tag{2}$$

The hydrogen ion that remains after hydrolysis immediately and instantaneously reacts with carbonate to form bicarbonate:

$$H^+ + CO_3^= \rightleftharpoons HCO_3^- \tag{3}$$

Potassium is merely a spectator ion. It takes no part in any reactions and, beyond affecting the ionic strength of the solution and its non-ideality, potassium itself has no effect on the solubility of CO_2 in Hot Pot solutions. The vapour-liquid equilibrium associated with the solubility of CO_2 in Hot Pot is modelled in the ProTreat® simulator on the basis of a concentrated solution of electrolytes.

The rate of the CO_2 hydrolysis reaction (Reaction 2) is fairly slow because the OH^- ion concentration is low, and CO_2 is a sparingly soluble gas. This leads to quite tall absorption and regeneration towers without a promoter. DEA is a secondary amine and reacts readily with CO_2, so its addition to carbonate solutions tends to speed up the absorption process. DEA reacts with CO_2 according to the mechanism:

$$CO_2 + R_2NH \rightleftharpoons R_2NH^+COO^- \qquad (4)$$

$$R_2NH^+COO^- + R_2NH \rightleftharpoons R_2NH_2^+ + R_2NCOO^- \qquad (5)$$
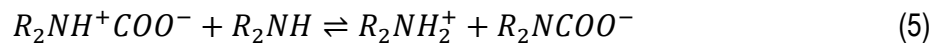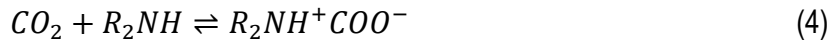
Reaction (4) occurs at finite rate while Reaction (5) involves only a proton transfer and so is instantaneous. Apart from the molecular species CO_2, DEA, and of course water, the solvent again is an electrolyte soup and when combined with Hot Pot, the correct way to determine CO_2 solubility is with an electrolyte model. This is the way ProTreat simulation does phase equilibrium calculations.

The amine of choice for promoting Hot Pot is DEA. As a secondary amine, DEA binds less strongly to CO_2 so carbamate decomposition in the regeneration step requires less energy. MEA reacts faster with CO_2, which for the same molar concentration would enhance the absorption rate; however, the cost is a higher regeneration energy requirement compared to DEA, and MEA's absorption rate advantage can be easily achieved using DEA with a small amount of additional packing. As will be seen, a small amount of DEA also lowers the CO_2 equilibrium backpressure over the treating solution.

Fractional Conversion

Fractional Conversion, F_c, is the extent to which a carbonate solvent is saturated with CO_2:

$$F_c = \frac{½[KHCO_3]}{[K_2CO_3]_O}$$

If the solvent is promoted with DEA, then Fractional Conversion is:

$$F_c = \frac{½[KHCO_3] + [DEACOOH]}{[K_2CO_3]_O + [DEA]_O}$$

The subscript 'o' signifies the concentration of the component in the completely CO_2-free state, i.e., the fresh solvent before it has been exposed to carbon dioxide. $DEACOOH$ is equivalent to R_2NCOO^- in Equation (5). These definitions are the exact equivalents of the term 'loading' as used with amines in the natural gas industry.

Effect of DEA on Equilibrium Solubility of CO_2 in Hot Pot

The ProTreat® simulator was used to develop solubility curves for CO_2 in Hot Pot with and without DEA. The cases considered were 30 wt% K_2CO_3 and 30 wt% K_2CO_3 + 2.5 wt% DEA because the latter corresponds to the solvent formulation in the case study to be considered later. Figure 1 shows the extent to which 2.5% DEA reduces the CO_2 backpressure at absorber lean-end conditions. Fractional

Conversions between 0.1 and 0.25 have CO_2 levels in the gas between 100 and 3,000 ppmv. There, 2.5 wt% DEA reduces equilibrium CO_2 pressures between 10 and 40% (i.e., the ppmv ratio is 0.6–0.9).
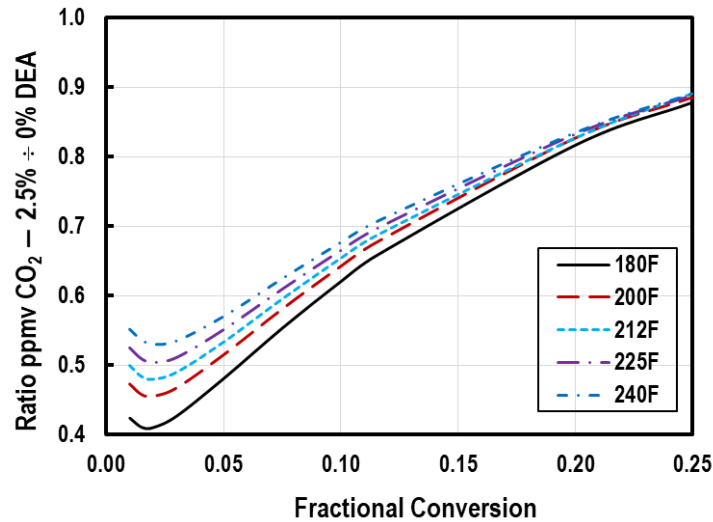

Figure 1   **Effect of DEA on CO_2 in Gas at Equilibrium, Shown as the Ratio of ppmv CO_2 without DEA to ppmv CO_2 with 2.5 wt% DEA**

Case Study – 1,000 MTPD Ammonia Plant

The case study is based on a 1,000 MTPD ammonia plant. The CO_2 section uses the two-stage DEA-promoted Hot Pot system shown in Figure 2. The simplified drawing omits several energy conservation measures but retains the features essential to the discussion. Table 1 shows the parameters pertinent to the raw gas (Stream 3).

Table 1   Condition of Gas Entering Absorber (Dry Basis, Stream 3)

Parameter	Value
Temperature, °C	124
Pressure, barg	31
Flow, 1000's Nm³/h	160
Composition, mole %	
Carbon Dioxide	17.4
Methane	0.90
Hydrogen	60.6
Carbon Monoxide	0.17
Nitrogen	20.7
Argon	0.23

Process Gas to Methanator

Washwater

Absorber

Lean Recycle

8

11

9

52

7

Semi-Lean Recycle

3

Hot Crude Gas

14

Cooler/Separator

6

Controller

CB

12

PRV

10

Lean Pump

Semi-lean Pump

13

17

To Water Stripper

2

CO2 to Urea
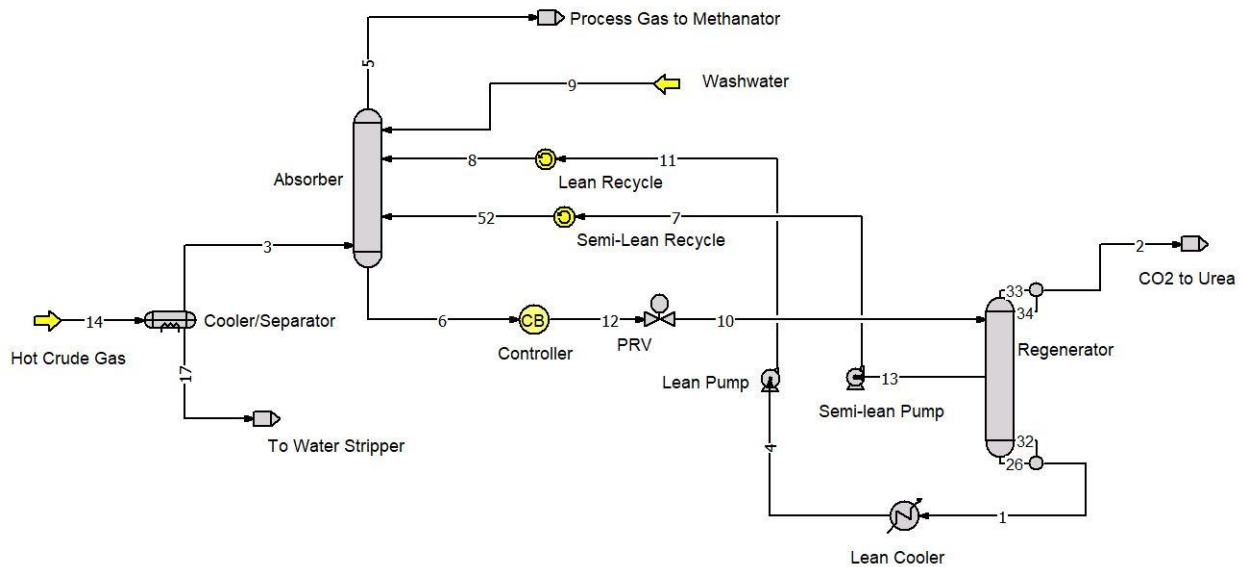
33

34

Regenerator

32

26

1

Lean Cooler

Figure 2   Simplified Schematic of Two-stage CO₂ Removal System

Both towers contained more than one type and size random packing in multiple beds. The absorber had two water wash trays at the top, and a total of 32 metres of packing distributed roughly equally between the lean (2,600-mm diameter) and semi-lean (4,250-mm diameter) tower sections. The regenerator was 5,000mm diameter above the semi-lean draw point holding 25.6 metres of packing and 3,050 mm diameter in the lean section with 18 metres of packing.

This plant actually operates with 30 wt% potassium carbonate and 2.5 wt% DEA and the ProTreat® simulator predicted performance parameters very close to measured data without the need for any adjustment or manipulation of *any* parameters to achieve agreement between simulation and measurement. In other words, the simulation is fully predictive without adjustable parameters. The same unit was simulated without DEA, all other parameters being identical between the two cases. The effect of DEA on overall performance of both absorber and regenerator is summarized in Table 2. Using 2.5 wt% DEA provides a very satisfactory synthesis gas.

Non-promoted Hot Pot leaves enough additional CO_2 in the treated gas to result in roughly a 7.4 MTPD loss in ammonia production. At the notional value of USD 300 per metric ton, this lost production is worth about USD 2,220 daily in unrealized revenue. However, hydrogen makeup and energy are additional costs and, when these are factored in, the cost of the additional CO_2 slip is really about USD 7,800 per day for this size plant. The question is what is happening in the columns to produce these not insubstantial differences.

Table 2   System Performance using Promoted vs. Non-promoted Hot Pot

	DEA-Promoted	Non-promoted
CO_2 in Treated Gas, ppmv	350	1,530
Lean Solvent Fractional Conversion	0.116	0.203
Semi-Lean Fractional Conversion	0.541	0.563
Rich Solvent Fractional Conversion	0.691	0.739

Absorber

Figure 3 shows and compares how CO_2 concentration is changing across the absorbers in the two cases. Apart from the obviously lower CO_2 slip with DEA promotion, there are several other observations worth noting.

Firstly, regardless of promotion, the full benefit of using a semi-lean stream is realized in the bottom five metres of packing—the next 12 metres do absolutely nothing towards removing CO_2. Also the benefit of promotion is fairly small in the semi-lean section because the Fractional Conversion is already high there, so most of the DEA has already been converted to carbamate.
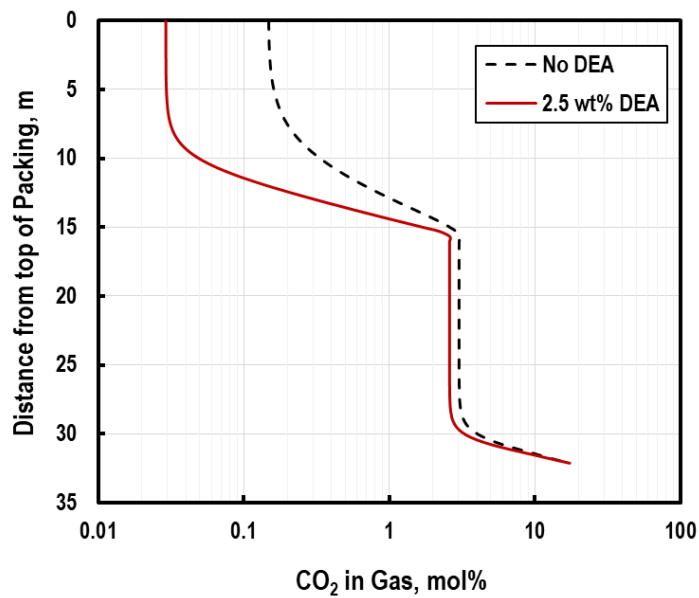

Figure 3   How CO_2 Concentration Changes through the Absorber (*note log scale*)

The differences in the lean section of the absorber are more striking. Without DEA promotion, CO_2 continues to be slowly removed across almost the entire lean (polishing) section. However, the addition of 2.5 wt% DEA drops the CO_2 concentration to 350 ppmv so quickly that the top five metres of packing are not even needed. Of perhaps greater value is knowing that the lean section is completely lean end pinched. This means simply that the final treating is determine by the lean solvent's Fractional Conversion. If there is enough packing in the absorber and the split between lean and semi-lean sections is properly chosen, this will almost invariably be the case. This absorber (probably like many Benfield absorbers) is over-packed and over-height by about a factor of two; however, these profiles suggest that where one's attention should be focused is on the regenerator because it is there that the lean and semi-lean solvents are produced.

Regenerator

Figure 4 shows how CO_2 strips out and reduces the Fractional Conversion to the lean solution value as the solvent flows through the regenerator. In both cases a large fraction of the dissolved CO_2 in the loaded solvent flashes off in the PRV (21.4% when promoted, 24.7% when not). As the solvent flows down the top 25 metres of packing, no stripping at all takes place—the upper section might as well not be there! The primary reason for this is that the stripping steam is metered to provide proper stripping of the 10% of the total solvent flow that actually reaches the lean section. The other 90% gets withdrawn as semi-lean solvent, having contacted a completely inadequate stripping steam flow, quite incapable of having a significant effect.
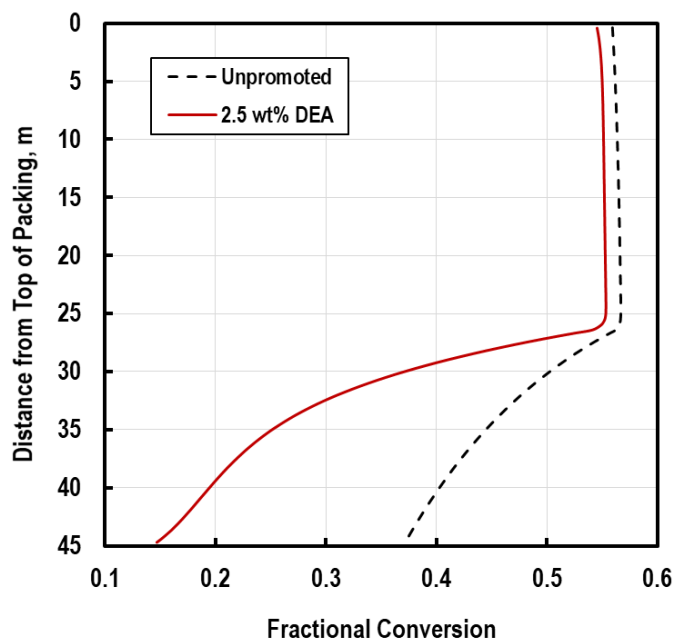
**Figure 4   Promotion with DEA Greatly Improves Regeneration.
Note that there is Additional Stripping in the Regenerator**

Below the semi-lean draw point the vapour-to-liquid flow ratio is high enough for the stripping vapour to actually strip CO_2 from the solvent. However, it is easy to see from Figure 4 that CO_2 strips from DEA-promoted Hot Pot a lot more easily than from its unpromoted equivalent. With the unpromoted solvent, there are no reactions to enhance mass transfer—stripping is purely a physical process. With DEA promotion, however, the decomposition of DEA carbamate enhances the mass transfer rate of stripping by factors of from four in the semi-lean section up to 70 at the bottom of the lean section, and the lower the Fractional Conversion, the greater the enhancement to the stripping rate. Thus, the Fractional Conversion of the fully stripped DEA-promoted solvent is roughly one-half the unpromoted value (0.116 versus 0.203).

Synopsis

There are a number of little-known (perhaps unknown) characteristics of Hot Pot and DEA-promoted Hot Pot that have a profound effect on the potential economics and efficacy of CO_2 removal using standard Hot Pot and Benfield processes. This article has discussed only one specific example of the CO_2 removal section of an ammonia plant; however, the operating conditions are fairly typical, and the observations and conclusions have general validity. In particular the ProTreat® mass transfer rate-based simulator was used to show the effect of spiking a 30 wt% Hot Pot solvent with 2.5 wt% DEA on (1) CO_2 solubility, (2) absorber performance, and (3) regenerator performance:

- The equilibrium CO_2 partial pressure over the promoted solvent may be as low as one-half the value in the unpromoted case. However, the effect is already weakening when Fractional Conversions approach values typical of treating with Hot Pot and Benfield technologies ($F_c \approx 0.1$), and it weakens further as Fractional Conversions go even higher. Nevertheless equilibrium pressures at the absorber lean end can be 25% lower when DEA is used as a promoter.
- The main effect of DEA is on the mass transfer (absorption and stripping) rates in both the absorber and regenerator.
- In an absorber, only the bottom few metres of packing in the semi-lean (bulk removal) lower section are useful for CO_2 removal. About the upper two-thirds provides no treating whatsoever.
- In the lean (gas polishing) upper section of the absorber, using DEA can reduce the amount of packed height needed for treating or it can extend the lean-end pinch region to insulate the column from process upsets. Even without DEA, the entire polishing section performs useful work.
- Benfield absorbers sometimes contain at least twice the amount of packing that is actually needed.
- In a lean-end pinched absorber, the quality of the treated gas is determined almost solely by the Fractional Conversion of the lean solvent, i.e., by regenerator performance, provided other operating conditions are what they should be.
- In the case examined here, the regenerator section used to produce semi-lean solvent could as well be replace by a flash drum, saving about half the tower height.
- The presence of DEA allows the Fractional Conversion of the fully-lean to be reduced by a factor of two. This permits much cleaner syngas to be produced without incurring more than the cost of the additive.

With the exception of the effect of DEA on equilibrium CO_2 partial pressure, all the other findings are a direct result of using the ProTreat simulator's true mass and heat transfer rate-basis in the analysis. Without doing these calculations on a rate basis, none of these observations could have been made. There is no substitute for a simulator that does all calculations rate-based, without approximations or simplifications.

Perhaps the most important finding is that if the CO_2 unit is properly designed, what really determines treated gas quality is the performance of the regenerator, which can be greatly improved by using DEA as a promoter.