

# CO<sub>2</sub> Removal from Syngas Using Piperazine-Activated MDEA and Potassium Dimethyl Glycinate

R. Scott Alvis\*, Nathan A. Hatcher & Ralph H. Weiland  
Optimized Gas Treating, Inc.  
12337 Jones Rd., Suite 432  
Houston, TX 77070

## ABSTRACT

Although methyldiethanolamine, MDEA, can be activated by a number of amines, piperazine is the most commonly used promoter in applications involving CO<sub>2</sub> removal from syngas, as well as from natural gas in LNG production. Because of its very low regeneration energy, removing CO<sub>2</sub> using MDEA alone would be preferred; however, the reaction in solution is extremely slow and the absorption process is controlled entirely by resistance to mass transfer in the solvent phase. Piperazine is highly reactive with CO<sub>2</sub> (about ten times faster kinetics than monoethanolamine) which greatly enhances CO<sub>2</sub> absorption rates. Yet because only relatively small concentrations of piperazine are needed, solvent regeneration energy requirements are not much higher than for MDEA alone.

As part of a review of a solvent change-out from amine promoted hot potassium carbonate to piperazine active MDEA, this paper addresses the effects of such parameters as total solvent strength, piperazine-to-MDEA ratio and treating temperature and pressure on the treated gas CO<sub>2</sub> content and the necessary regeneration energy. It also compares piperazine-activated MDEA with piperazine-activated Alkazid DIK (potassium salt of the amino acid dimethyl glycine, KDiMGly) as a potential solvent for CO<sub>2</sub> removal applications. Alkazid DIK is a solvent used since the mid-1930s for H<sub>2</sub>S removal in refinery and coal gas applications but it fell out of favour with the advent of MDEA. It is completely nonvolatile and may be more oxidation resistant than the conventional amines.

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\*Speaker

## INTRODUCTION

In the early days of ammonia production, monoethanolamine (MEA) was commonly used for CO<sub>2</sub> removal from the synthesis gas using the Girbotol process. Somewhat later, hot potassium carbonate (the Benfield, or Hot Pot process) was used, often in a split flow configuration described as a two-stage Benfield LoHeat process for energy conservation. In the last 20 years, a very substantial fraction of these plants have been retrofitted using BASF's aMDEA process.

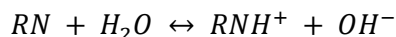
*N*-Methyldiethanolamine (MDEA) is a tertiary amine whose amino group is incapable of reacting with CO<sub>2</sub>. However, it is alkaline and so is an excellent sink for protons produced by CO<sub>2</sub> hydrolysis. Because it is non-reactive, aqueous MDEA by itself absorbs CO<sub>2</sub> far too slowly to be an effective solvent for treating ammonia synthesis gas. But when spiked with a relatively small concentration of piperazine, a diamine that reacts extraordinarily fast with CO<sub>2</sub>, the resulting blend is an excellent solvent for treating syngas and removing CO<sub>2</sub> in the production of LNG.

In this paper, we first present the results of a quantitative study of the piperazine promotion of MDEA, specifically the effects of piperazine to MDEA ratio, total amine strength, and the treating temperature on performance of a typical ammonia syngas CO<sub>2</sub> removal system. In a recent patent, Wagner et al. (2009) proposed using the alkali metal salts of a number of tertiary amino acids, appropriately promoted with reactive amines such as MEA. Some of the potentially more interesting results of our study include the utility of operating at higher temperatures with lower rather than higher total amine concentrations, and the existence of operating boundaries that can lead to unstable operation when approached too closely.

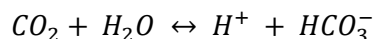
Following a discussion of amino acids and their mode of operation, we critically analyze the possibility of using the potassium salt of the tertiary amino-acid dimethylglycine, promoted with piperazine as a syngas treating solvent. The results show that it is possible to treat syngas quite effectively using such a solvent but with much lower concentration of the piperazine promoter. Furthermore, results suggest that the cross-exchanger commonly used as a heat integration tool in treating plants can be completely eliminated.

## USING TERTIARY AMINES FOR CO<sub>2</sub> REMOVAL

Before looking at specific chemical solvents, it is beneficial to describe the function of an amine that is completely nonreactive towards CO<sub>2</sub>, in the CO<sub>2</sub> absorption process, and to give a quantitative picture of how effective piperazine really is. Like all amines, tertiary amines dissociate in water and produce hydroxyl ion:



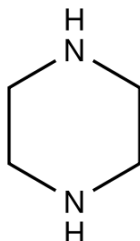
The hydroxyl ion is what gives amines their alkalinity. However, CO<sub>2</sub> does not react with a tertiary amino group because this group lacks the mobile hydrogen necessary to exchange for the CO<sub>2</sub> and form carbamate. Instead, the CO<sub>2</sub> merely absorbs into water and hydrolyzes:



The liberated proton is neutralized by the amine's alkalinity as represented by the hydroxyl group. Thus, unless one can directly catalyze the hydrolysis reaction itself (as can be done using carbonic anhydrase, for example), CO<sub>2</sub> absorption rates are not enhanced at all by reaction and will be *no faster than they would be into essentially pure water*. The function of the tertiary amine then, is *not* to enhance absorption rates through chemical reaction but rather to increase dramatically the *capacity* of the

solvent. The trouble with straight MDEA, however, is that the CO<sub>2</sub> absorption rate is almost always too slow for it to be used alone, except for bulk CO<sub>2</sub> removal at high pressure. It simply cannot be used effectively for the deep CO<sub>2</sub> removal required for syngas and LNG production. The CO<sub>2</sub> reaction must be promoted, and piperazine is an excellent promoter.

Piperazine is a cyclic diamine with the structure shown in Figure 1. It reacts with CO<sub>2</sub> about ten



**Figure 1 Piperazine**

times faster than MEA. Its second order rate constant at 25°C, for example, is about 59,000 L·mol<sup>-1</sup>·s<sup>-1</sup> versus MEA at 6,000 L·mol<sup>-1</sup>·s<sup>-1</sup>. This makes piperazine the most reactive promoter of CO<sub>2</sub> kinetics available commercially. Over the last 30 years, the aMDEA<sup>®</sup> process, first patented by BASF in 1982, has captured the lion's share of the ammonia syngas purification market, and it is still used in the majority of the world's ammonia plants.

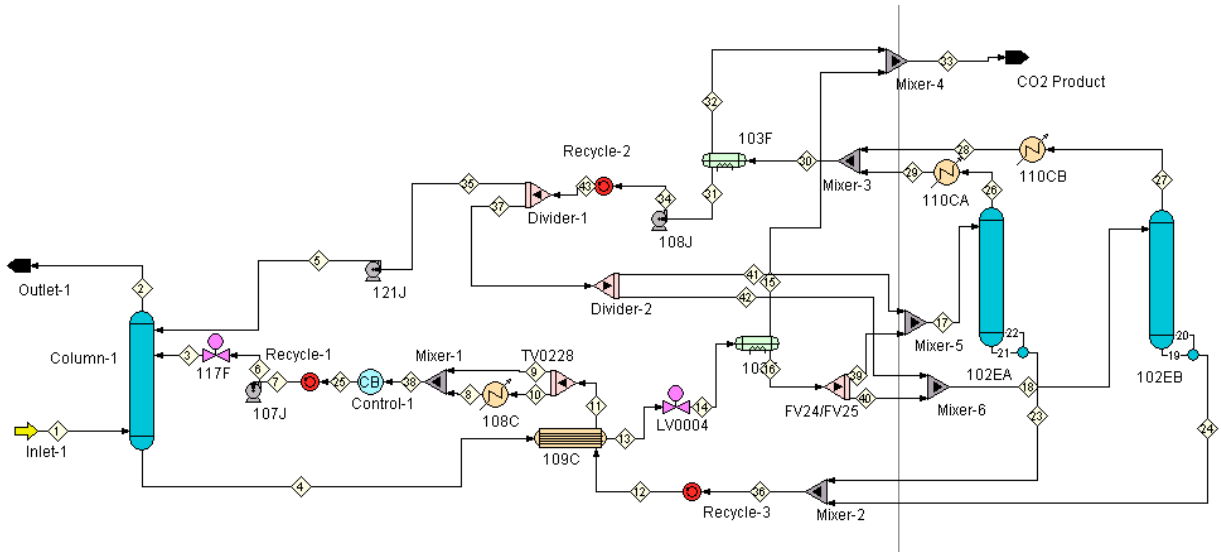
In summary then, although MDEA alone can be used for *bulk* CO<sub>2</sub> removal at high pressure, its reaction rate with CO<sub>2</sub> is much too slow for it to be usefully applied to *deeper* CO<sub>2</sub> removal in columns of reasonable height. For that, an activator is required, and piperazine has evolved as the activator of choice. Today, most solvent vendors offer a form of piperazine-promoted MDEA under a variety of brand and code names.

### DEEP CO<sub>2</sub> REMOVAL USING AN MDEA-BASED SOLVENT

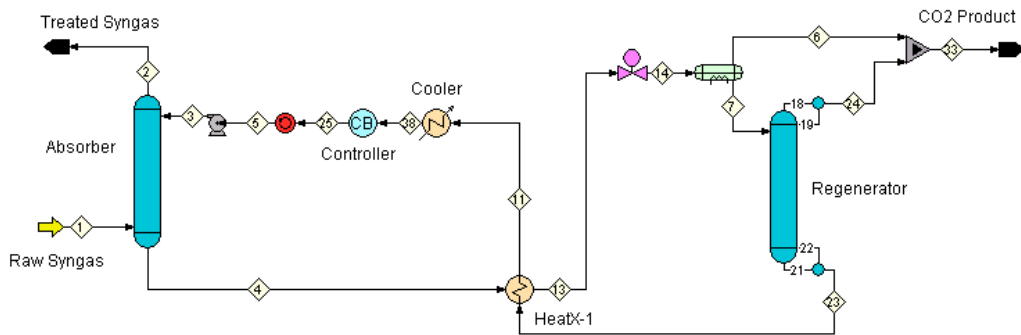
Using an amine process simulator that is founded upon real, mass and heat transfer rates allows a virtual plant to be constructed on a computer. In the present work, the ProTreat<sup>™</sup> simulator was used. ProTreat is the world's only true mass transfer rate-based commercial simulator dedicated to gas treating. A virtual plant built using ProTreat allows one to experiment with a wide variety of different process configurations and what-if scenarios. It is relatively easy to learn a great deal about a particular plant's performance characteristics and quantitatively understand how numerous plant operating parameters affect that performance. In what follows, we have used ProTreat to answer such questions as, "What is the best solvent concentration and formulation to use?" and "How does the treating temperature affect performance?". Although no public-domain plant data exist, or are available to us on the use of DiMGly as a solvent for syngas purification, a rather limited amount of fundamental data on vapor liquid equilibrium and physical properties is sufficient to determine a great deal about how this chemical will perform in a syngas treating situation. But that is for the next section of the paper.

A ProTreat PFD of the amine section of a typical ammonia syngas plant is shown in Figure 2. It has a single absorber but there are identical-twin regenerators in parallel. There is also a rather complex scheme for returning part of the condensate from the regenerator overhead condensers to a short wash section in the absorber for recovering amine vapors. The flowsheet is quite a bit more complex than needed to illustrate the main points of the paper so it has been greatly simplified to the PFD shown in Figure 3. The simplified flow sheet has a single regenerator, and we have eliminated any

consideration of an amine recovery section atop the absorber. The plant was designed to treat 208 000 NCMH raw gas at 26.4 bara and 37°C containing 60.2 mol% H<sub>2</sub>, 20.9 mol% N<sub>2</sub>, and 17.9 mol% CO<sub>2</sub> with the balance being trace amounts of argon, methane, carbon monoxide, and water vapor. For this study, the absorber was packed with 15.25 m (50 ft) of #50 IMTP tower packing. The regenerator was also packed, and contains 10.4 m (34 ft) of #3 Cascade Mini-rings. Although this absorber had a little deeper packed bed than found in many syngas CO<sub>2</sub> plants, the conclusions of the paper are in no way affected.



**Figure 2 Original Amine Treating Unit for Ammonia Syngas**

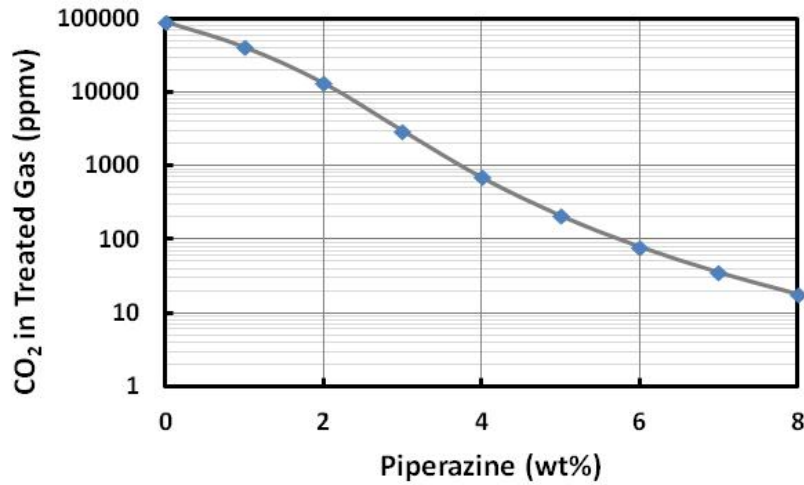


**Figure 3 Simplified Syngas Treating PFD**

### MDEA-Piperazine Composition

The most commonly used total-amine strength for generic MDEA and MDEA-based blends is 50 wt% although, as we shall see, this is sometimes not the best concentration to use. Figure 4 shows how the relative concentrations of piperazine and MDEA in a 50 wt% total-amine blend affect the CO<sub>2</sub> left in the treated gas. It is apparent from the figure that about 4 wt% piperazine is needed to achieve < 1 000 ppmv CO<sub>2</sub> and that 5 or 6 wt% piperazine allows one to achieve in the vicinity of 100 ppmv CO<sub>2</sub>. The treating performance is very sensitive to the concentration the piperazine additive and this is why it is so important to monitor solution strength for piperazine content. Unfortunately, piperazine is somewhat

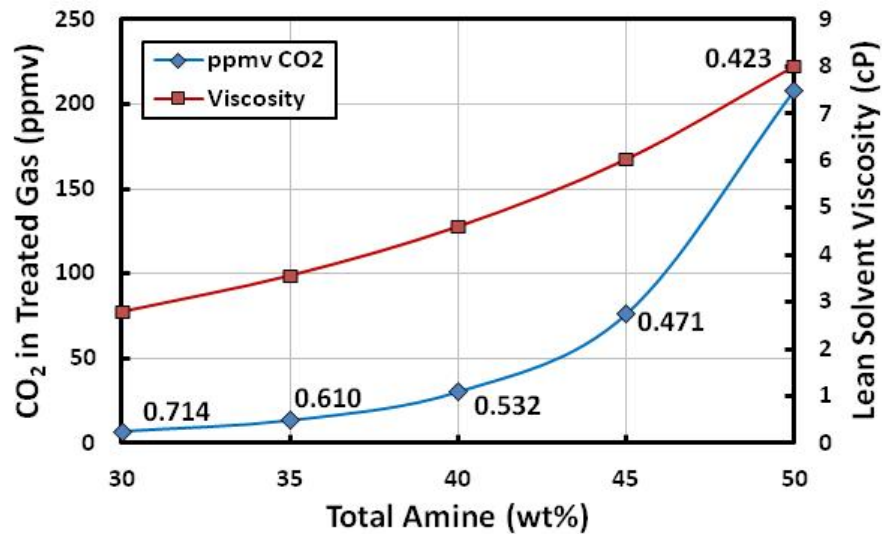
volatile so its concentration tends to fall with time more rapidly than does MDEA. Plant performance depends critically on maintaining the right concentrations of the solvent ingredients.



**Figure 4** Effect of Piperazine concentration in MDEA (Total 50 wt% amine) on CO<sub>2</sub> Level in Treated Syngas

### Solvent Total Amine Strength

Having established that this plant will operate quite comfortably with 5 wt% piperazine and 45 wt% MDEA, we then asked the question, what effect does total amine strength have on the CO<sub>2</sub> content of the treated gas? Figure 5 summarizes the findings. The numbers next to points on the ppmv CO<sub>2</sub> curve are the corresponding CO<sub>2</sub> mole loadings (per mole total amine) of the rich solvent from the absorber.



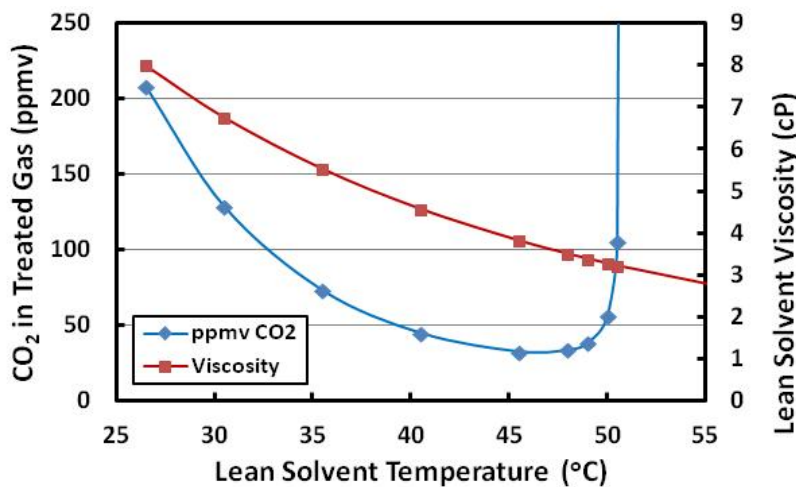
**Figure 5** Effect of Total Amine Strength on CO<sub>2</sub> Level in Treated Syngas and on Solvent Viscosity

It might be surprising that the higher the amine strength the *worse* the treating. Using 50 wt% total amine (Base Case), the simulated treated gas has 208 ppmv CO<sub>2</sub> and a very satisfactory rich solution loading of 0.423 moles CO<sub>2</sub> per mole of total amine. However, 45 wt% amine allows a 75 ppmv CO<sub>2</sub> gas to be produced and 40 wt% amine reduces the CO<sub>2</sub> to about 30 ppmv. With 30 wt% amine the residual CO<sub>2</sub> is even lower. However, on the negative side, the rich solution loading increases to unacceptably high levels from a carbon-steel metallurgy corrosion standpoint. Of course, stainless cladding in the right places, and the use of stainless exchanger bundles, would overcome this objection.

The reason for improved treating with lower solvent strengths is the lower solvent viscosity that accompanies reduced amine concentration. CO<sub>2</sub> absorption is a process whose rate is controlled by mass transfer resistance in the liquid, or solvent, phase, and the more viscous that phase is, the greater the resistance. As Figure 5 shows, dropping amine concentration from 50 wt% to 30 wt% reduces solvent viscosity by a factor of nearly three. This allows CO<sub>2</sub> to be absorbed faster and allows the 15<sup>+</sup> metres of packing to extract enough extra CO<sub>2</sub> to reduce the treated gas concentration from 208 ppmv to just a little over 7 ppmv. Solvent viscosity is an important factor in absorber performance, and any successful effort to lower it will pay dividends. Another way to lower viscosity is to use a hotter solvent.

### Solvent Temperature

As Figure 6 shows, setting the solvent temperature at 50°C, say, rather than 26°C lowers the viscosity by a factor of nearly three as well, and treating improves dramatically over the Base Case. The simulated results shown in the figure are for a 45 wt% plus 5 wt% piperazine solution. Treated gas CO<sub>2</sub> content drops rapidly with temperature but eventually it levels out, then experiences a precipitous rise. In this case, a temperature of just over 50°C presents an operational cliff. As temperature rises, of course, the vapor pressure of CO<sub>2</sub> over the solvent goes up as well, and near 50°C the point is reached where reduced solubility prevents absorption of enough CO<sub>2</sub> even to come close to meeting a < 1 000 ppmv CO<sub>2</sub> specification. The ppm CO<sub>2</sub> level suddenly rises because the solvent's capacity has been reduced to a level insufficient to absorb enough CO<sub>2</sub>. The excess CO<sub>2</sub> in the inlet simply passes right through the column and CO<sub>2</sub> breakthrough is experienced. Operationally, it would be very dangerous to operate too close to this temperature because it would become impossible to maintain control of outlet CO<sub>2</sub> levels.

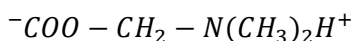


**Figure 6** Effect of Solvent Temperature on CO<sub>2</sub> Level in Treated Syngas and on Solvent Viscosity

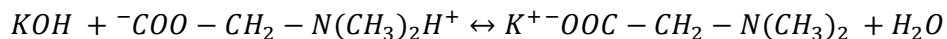
## AMINO ACID SALT BASED SOLVENT — POTASSIUM DIMETHYLGLYCINATE (KDiMGly)

Potassium dimethylglycinate is the potassium salt of dimethyl glycine, and was known under the BASF trade name Alkazid DIK. This is a tertiary amino acid salt that since 1935 had been used quite successfully and extensively, mainly in Europe, for selectively removing H<sub>2</sub>S from such problematic streams as refinery and coke oven gases. These gases tend to be heavily contaminated with various components known to be hard on conventional amines. With the advent of MDEA, its use diminished, and eventually it stopped being offered commercially. However, KDiMGly has certain properties such as zero vapor pressure and possibly oxidation resistance that are making it more attractive in post-combustion CO<sub>2</sub> capture, and which may make it a useful alternative to MDEA for ammonia syngas.

As the name implies, amino acids contain an amino group at one end of the molecule and a carboxylic acid group at the other. In aqueous solution, dimethyl glycine exists as a so-called zwitter ion:

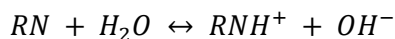


Because the amino group is protonated, it is completely nonreactive towards CO<sub>2</sub> and it is pH neutral which, from the standpoint of life on earth, is probably a good thing. But as a solvent for CO<sub>2</sub> it is virtually useless, having neither reactivity nor absorption capacity. However, when the acid group is titrated (neutralized) with KOH the amino group deprotonates,



and produces what is now an alkaline, tertiary amine. An important property is that KDiMGly and all other amino acid salts exist in water as fully-dissociated salts, making them completely non-volatile. Furthermore, amino acids are already partially oxidized which *may* give them better resistant to further oxidation.

In the case of KDiMGly, the two additional methyl groups are attached to nitrogen at the amino end of the molecule, depriving the amino group of the proton necessary for reaction with CO<sub>2</sub>. The amino group is tertiary; however, is it nonetheless highly alkaline in the same was as MDEA and, in solution, dissociates according to



Just as for MDEA, tertiary amines do not react with CO<sub>2</sub> (no carbamate or other reaction products with the amine are formed) so the CO<sub>2</sub> absorption rate will be nearly identical with what it would be in water, i.e., extremely slow. But the alkalinity gives the solvent high CO<sub>2</sub> holding capacity, if only the CO<sub>2</sub> could get into solution in the first place. This is done by promoting the solvent with very fast-reacting piperazine.

### Model Studies of the KDiMGly-Piperazine Solvent

Because chemicals are bought and sold by weight, we are used to thinking about solvent strength in terms of the weight percent of the active ingredients. However, chemistry works on the basis of moles. To do as nearly a one-to-one comparison with piperazine-promoted MDEA as possible it is necessary to use equal *molar* concentrations of the main constituent, and it turns out that 54.25 wt% KDiMGly is equivalent to 50 wt% MDEA. Therefore, this was the base concentration used in the amino acid study.

#### KDiMGly-Piperazine Composition

Figure 7 shows that even without the piperazine additive, KDiMGly removes more CO<sub>2</sub> (6.96 mol% CO<sub>2</sub> in the treated gas) than the MDEA molar equivalent (9.068 mol% CO<sub>2</sub>). This suggests higher driving force for absorption (low vapor pressure of CO<sub>2</sub>) when KDiMGly is used in a plant operating under otherwise identical conditions of solvent rate, reboiler duty, equipment details, and so on.

Considerably less piperazine (2 wt% versus 4 wt%) is needed to achieve 1 000 ppmv treated gas, and the response to piperazine addition is higher. Lower piperazine concentrations mean reduced potential vaporization losses and, of course, the completely nonvolatile nature of KDiMGly eliminates this inventory loss mechanism.

### Effect of Total Amine Strength

Lower total amine concentration is simulated to have an effect similar to MDEA, although the viscosity reduction is not as great (a factor of two versus a factor of three for MDEA) and therefore the impact of lower total amine concentration is not as great. Figure 8 shows the simulation results. The numbers beside each simulation data point are the rich solution CO<sub>2</sub> loading values, which are higher than corresponding rich loadings for MDEA. KDiMGly is harder to strip than MDEA because for the same loading value the CO<sub>2</sub> vapor pressure is lower. In other words, because of its higher pH (e.g., 12.05 for 54.25 wt% KDiMGly versus 11.72 for 50 wt% MDEA, both at 26.5°C) KDiMGly has higher affinity for CO<sub>2</sub> than MDEA does. The lean solution loading for piperazine activated MDEA is typically 0.003 but for KDiMGly under similar conditions it is 0.13; the question is whether a difference of 0.13 loading units makes a KDiMGly solution more corrosive than MDEA under the same conditions. Because it is bicarbonate that is responsible for corrosion, the answer is probably yes, and some stainless metallurgy in vulnerable sections of process equipment and piping would be prudent. However, there is another significant benefit to be gained from using piperazine-promoted KDiMGly.

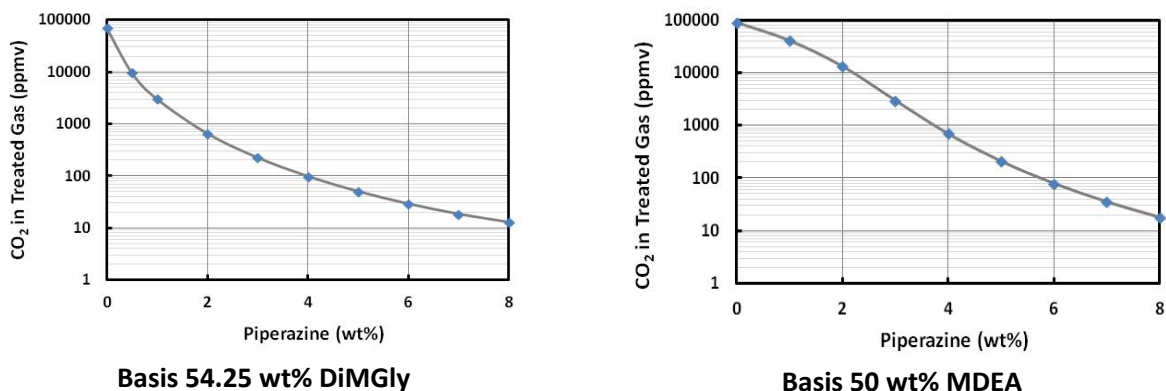


Figure 7 Effect of Piperazine Concentration on CO<sub>2</sub> Level in Treated Syngas

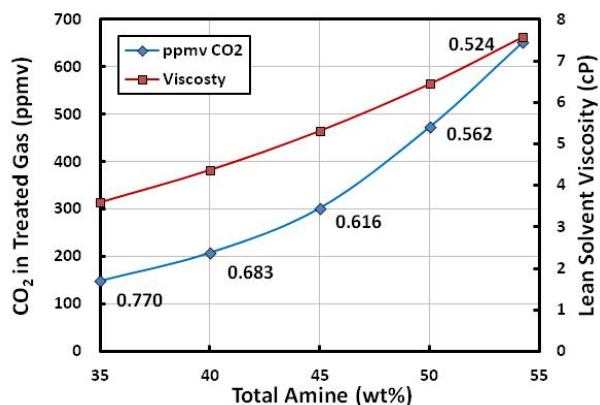


Figure 8 Effect of Total Amine Strength on CO<sub>2</sub> Level in Treated Syngas and on Viscosity of KDiMGly



### Effect of Treating Temperature Using KDiMGly

As shown in Figure 9, higher solvent temperatures (lower viscosity solvent) lead to significant improvements to the residual CO<sub>2</sub> concentration in the treated gas. Unlike the MDEA-based solvent, there is no precipitous loss of performance when the temperature reaches high values. Instead, there is a broad minimum in the treating performance curve. This results from the competing effects of increasing absorption rates (from diminished solvent viscosity), versus increasing equilibrium CO<sub>2</sub> vapor pressure (reduced driving force for absorption) with higher temperatures. Solvent temperatures anywhere between 35 and 85°C permit very satisfactory treating; however, the ability to use a high temperature solvent offers potential advantages.

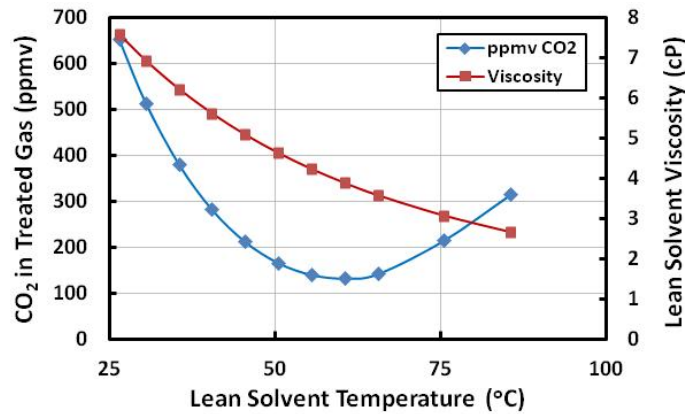


Figure 9 Effect of Solvent Temperature on CO<sub>2</sub> Level in Treated Syngas and on KDiMGly Viscosity

### Advantages to Treating with Hot Solvent

Figure 10 shows how lean amine temperature affects the temperature of the rich solvent leaving the absorber. Here one can see that in the present case, for a lean amine temperature of 85°C, the rich amine will be at nearly 105°C. This means that the rich solvent requires no preheating to ensure it enters the stripper at a reasonable temperature. The cross exchanger can be completely eliminated from the plant, and this would be possible even with a lean solvent temperature of 60°C where the best CO<sub>2</sub> removal is achieved. The ability to run hot has a certain parallel with the HotPot process but does

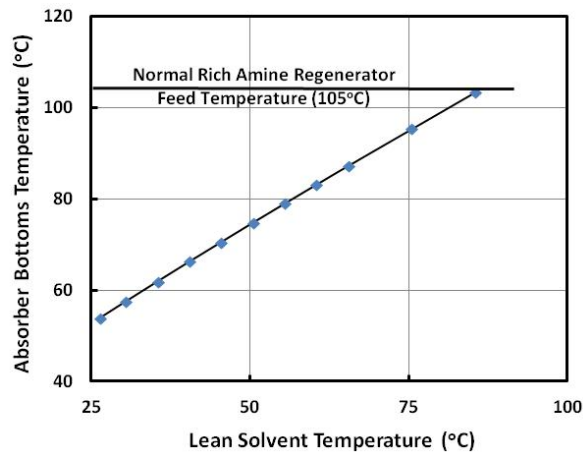


Figure 10 Effect of Lean Solvent Temperature on Rich Amine Temperature

not need a semi-lean process flow sheet configuration. Instead, the process flow sheet is even simpler than for conventional amine treating.

Piperazine-promoted KDiMGly appears to be a viable option for CO<sub>2</sub> removal from ammonia syngas. It's a question of whether the cost of better metallurgy (which may already exist in a piperazine promoted MDEA plant) exceeds the benefits of lower amine losses, smaller heat exchangers, and the elimination of the usually quite large cross exchanger.

## SUMMARY

Using minimal new data (some vapor-liquid equilibrium and pH data for determining amine dissociation constants together with estimated solution properties), a real mass and heat transfer rate-based amine simulator allows the construction of a virtual plant in software. The virtual plant is extraordinary versatile and capable of accurately predicting the performance of proposed units, without pilot planting or the gathering of field data, i.e., very inexpensively. Mass transfer rate-based modeling has been around since the mid-80s and is a fairly mature technology. The gas treating industry is now rapidly moving away from the tried and true, but antiquated, equilibrium stage approach, with its need for engineer-guessed efficiencies and transfer unit heights.

This contribution has show that with piperazine activated MDEA:

- One must be careful to monitor solution composition and control the piperazine level because performance is quite sensitive to this parameter,
- The maxim of always using 50 wt% total amine solvent is false, and significant improvements to treating levels can be realized by operating at lower concentrations. The 50 wt% rule should be examined in each and every case,
- When treating goals are not being met, using a colder amine may be a step in the wrong direction.
- Solution viscosity has a profound effect on CO<sub>2</sub> removal rates and whatever can be done to lower its value, consistent with other operating constraints, will be beneficial.

With KDiMGly there is potential to:

- Reduce heat exchanger surface areas.
- Eliminate the cross exchanger altogether.
- Lower potential amine vaporization losses.
- Perhaps use a more robust amine as the base for the solvent.

But when all is said and done, the real key to understanding and improving plant performance is the availability and use of a real mass transfer rate-based simulator.

## REFERENCES

Wagner, R., U. Lichtfers and V. Schuda, Removal of Carbon Dioxide from Combustion Exhaust Gases, Patent Application US 2009/0320682 A1, 31 December 2009.