Converting to DEA/MDEA Mix Ups Sweetening Capacity

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ABSTRACT

Mixing amines can be the best method for increasing capacity or improving efficiency in an amine sweetening unit. In many cases, it may be possible simply to add a second amine to the existing solution "on the fly", or as the unit is running.

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INTRODUCTION

Mixing amines can be the best method for increasing capacity or improving efficiency in an amine sweetening unit. In many cases, it may be possible simply to add a second amine to the existing solution "on the fly," or as the unit is running.

Union Pacific Resources' Bryan, Tex., gas plant provides one example. The plant was converted from diethanolamine (DEA) to a DEA/MDEA (methyl DEA) mixture after analysis by TSWEET, a process-simulation program.

After conversion, CO_2 levels in the sales gas fell to less than pipeline specifications. Data were taken for the absorber at a constant amine circulation of 120 gpm. A comparison of the performance data to the values calculated by the program proved the accuracy of TSWEET.

EXPANDING

In many gas-processing plants, the amine unit may limit the entire plant throughput because of, for example, increased acid-gas concentration in the feed or increased feed volume.

Increasing the unit's efficiency by converting from a single-amine solution to a mixture of amines most commonly involves use of a DEA/MDEA mixture.

The optimum solution concentration and ratio of amines depend on absorber pressure, acid-gas concentration in the feed, contactor operating temperature, and sweet-gas requirements (how much CO_2 slip is allowable).

A process simulator such as TSWEET can simplify the evaluation of adding a second amine.

Each amine has unique advantages and disadvantages.[1] For example, a primary amine (MEA) is more reactive with CO_2 than a secondary amine (DEA), which is in turn more reactive than a tertiary amine (MDEA or TEA).

In most cases, however, the maximum concentration and acid-gas loading of primary and secondary amine solutions are usually limited by corrosion problems. The most widely accepted solution concentrations are <20 wt % for MEA and <35 wt % for DEA.

A high concentration of MDEA in solution does not result in corrosion problems as do MEA and DEA. MDEA reacts slowly with CO_2 and is most commonly used where CO_2 slippage is desired.

Such operating parameters as longer liquid residence times on the absorber trays and higher absorber temperatures may be manipulated to accelerate CO_2 pickup by MDEA.[2]

MDEA has several advantages over primary and secondary amines including higher solution concentration, higher loading with fewer corrosion problems, lower heat of reaction leading to better stripping, higher resistance to degradation, and lower vapor pressure.[3]

Furthermore, MDEA is selective toward H_2S in the presence of CO_2. This selectivity results from the inability of tertiary amines to form a carbamate with CO_2.

MDEA does not have a hydrogen attached to the nitrogen and cannot react directly with CO_2 to form carbamate. MDEA can, however, react with H_2S by the same proton-transfer mechanism of primary and secondary amines.[4]

USING MIXED AMINES

The concept of using amine mixtures is based on utilizing and combining the advantages of the amines in the mixture or of customizing the amine solution to a particular use. Mixing MDEA with DEA, for example, can increase the total amine solution concentration without increasing corrosion problems.

The easiest and least expensive method of switching from a single amine to a mixed amine solution is simply to add the second amine "on the fly," while the unit is operating.

If, however, the amine unit has become dirty or the amine has degraded, switching amines presents an opportunity to shut down the unit, drain the system, and clean or replace equipment.

In this case, the unit should be reloaded with the target amine solution concentrations. If the concentrations do not meet the target, the appropriate amine may be added as necessary.

BRYAN PLANT

A recent example of a conversion to mixed amines is Union Pacific Resources' DEA-to-MDEA/DEA mixture at its

Bryan, Tex., gas plant.

As shown in Fig. 1, the feed-gas stream passes through a compression station to a standard refrigeration plant where liquids are extracted. The gas is sent to an amine unit for sweetening to a product specification of 0.35 mole % CO_2. Liquids must pass the copper 1A strip test for H_2S.

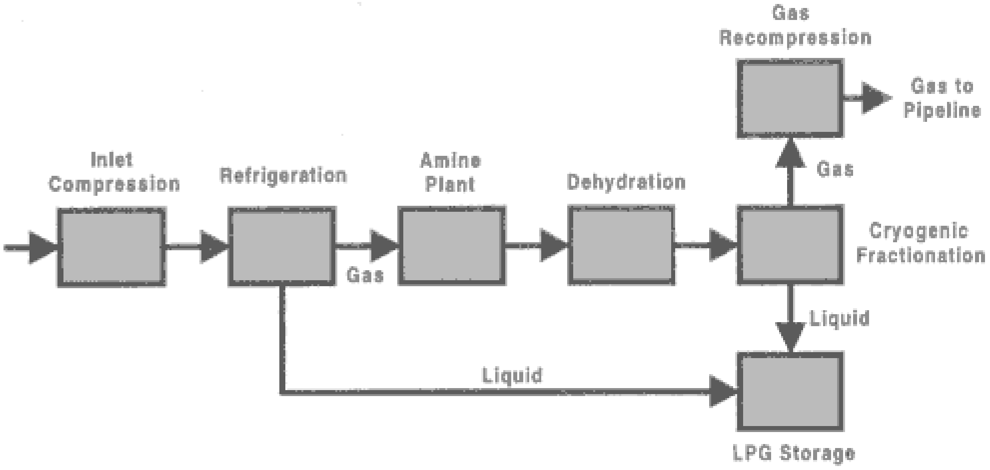


Figure 1. UPR's Bryan, Texas gas plant.

The Bryan gas plant (Fig. 2) was designed to process 35 MMscfd of gas containing 2.91% CO_2 and 0.06 gr/100 standard cu ft H_2S with 35 wt % DEA. The absorber is a 20 stage valve tray column with an amine circulation of 130 gpm.

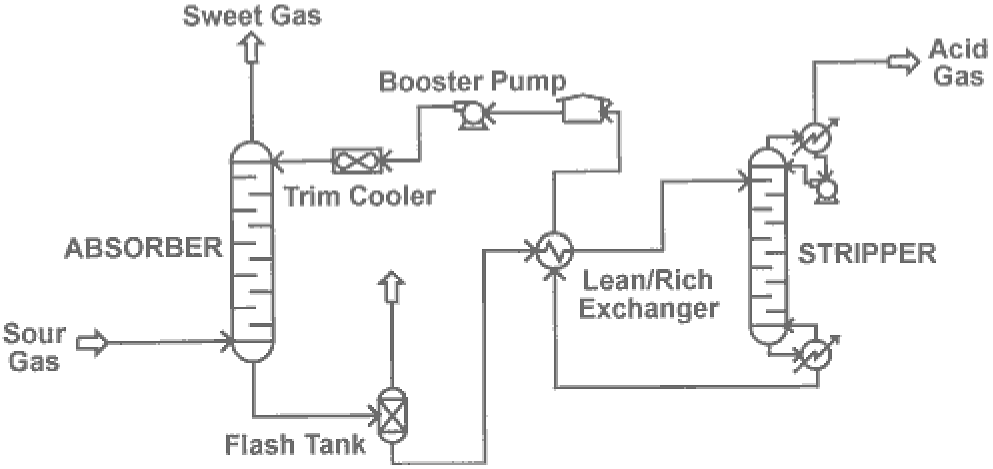


Figure 2. Bryan Plant's amine sweetening unit.

Since the plant was built in 1980, the CO_2 content in the inlet-gas stream continually increased until the amine unit could not handle the increased CO_2 concentration and the CO_2 gas product specification was not met. The amine unit became the plant bottleneck.

The rich amine loading has increased to 0.56 mole acid gas/1.0 mole amine which could lead to corrosion problems with DEA, and the CO_2 concentration in the sweet gas is as high as 0.42%.

To increase the capacity of the amine unit, Union Pacific Resources considered designing a parallel unit, increasing the circulation rate and adding a larger reboiler, and switching to a mixture of MDEA/DEA.

Adding a parallel unit would be very expensive.

Increasing the circulation rate of the DEA solution would require replacing the stripper reboiler and pumps throughout the plant. In addition to costs, this alternative would also require extended downtime.

The third alternative, adding MDEA to the existing DEA solution, would increase the CO_2 absorption without a significant increase in corrosion. Therefore, the addition of MDEA to the DEA solution warranted further investigation.

Although MDEA is known for selectively absorbing H_2S and rejecting CO_2, an increase in CO_2 absorption was desired in the case of the Bryan gas plant. Increasing the concentration of DEA alone would absorb additional CO_2 but would increase corrosion.

Addition of MDEA to raise the total amine solution concentration would increase CO_2 absorption but would not significantly affect corrosion levels.

The feasibility study was performed by the process simulation program TSWEET which models amine sweetening units. The program was developed by Bryan Research & Engineering Inc., Bryan, Tex., and uses the flexible flowsheet and operating concept.

Beginning with the process flowsheet and operating parameters, complete material and energy balances for steady-state operating conditions can be performed.

Rigorous tray-by-tray calculations using the Ishii-Otto method[5] design the stripper and absorber columns. Vapor pressures of H_2S and CO_2 over the amine solutions are calculated by the non-random, two-liquid (NRTL) equilibrium model.

A kinetic model is used to predict the effect of residence time, temperature, solution concentration, feed pressure, and type of amine on the rate of CO_2 absorption.

The program has been reliable in calculating the performance of amine gas sweetening plants.[6,7]

Based on the TSWEET program results, Union Pacific Resources concluded that with the addition of MDEA to the DEA solution, the existing equipment at the Bryan gas plant had sufficient capacity to absorb enough CO_2 to meet the sweet-gas specification and that no equipment modifications were necessary.

UPR decided to convert to a DEA/MDEA mixture.

CONVERTING, TESTING

There are two options for converting from DEA to a DEA/MDEA mixture. The conversion can be performed by adding the MDEA during operation without a plant shutdown, or the unit can be shut down, cleaned, and reloaded.

While shutting down the amine unit is not required, it may be a good idea if cleaning the system or replacing equipment is necessary. During amine conversion at the Bryan gas plant, Union Pacific Resources first chose to drain the system in order to replace a fouled heat exchanger.

The amine unit was taken off-line, cooled down, and drained to its low points. Next, the lean/rich exchanger was replaced and the unit was reloaded with a premixed amine solution.

The initial amine solution was 65 wt % water, 25 wt % DEA, and 10 wt % MDEA. The system was then put online and tested. Additional amine was gradually added until a final concentration of 50 wt % water, 35 wt % DEA, and 15 wt % MDEA was achieved.

The absorber performance at the plant was studied with a constant amine circulation rate of 120 gpm. Data were taken daily for the gas flow, composition, temperature, and pressure of the feed and exit gas, lean amine temperature, lean-amine loading, and sweet-gas composition.

Recorded stripper data included feed temperature, overhead temperature and pressure, pressure drop, and reboiler and condenser temperatures. All flow rates were measured by orifice meters and all temperatures were measured by calibrated thermocouples.

The acid-gas compositions were determined by titrimetric analysis. The remaining gas compositions were determined by gas chromatography.

PLANT PERFORMANCE

After switching to a DEA/MDEA mixture, the plant operated without problems. The concentration of CO_2 in the sweet gas was less than 1,000 ppm and as low as 200 ppm. Table 1 shows the inlet conditions to the absorber at each test date.

Table 1. Bryan Plant inlet conditions to absorber.

	Inlet Gas				Lean Amine			
Date, 1995	Flow MMSCFD	Temp ^{o}F	H_2S ppm	CO_2 %	Flow gpm	Temp ^{o}F	DEA wt %	MDEA wt %
Dec. 5	27.50	101.0	7	3.50	120	110.0	32.17	-
Dec. 6	28.50	102.0	7	3.25	120	112.0	31.73	-
Dec. 7	27.70	101.0	8	3.30	120	105.0	31.01	-
Dec. 9	26.30	103.0	8	3.50	120	120.0	31.56	-
Dec. 10	26.00	101.0	8	3.40	120	129.0	30.86	-
Dec. 11	26.20	101.0	8	3.50	120	125.0	31.86	-
Feb. 13	27.79	105.3	6	2.80	120	134.1	32.09	13.63
Feb. 14	26.21	105.3	8	3.20	120	127.0	32.42	13.74
Feb. 15	27.85	88.5	6	2.00	120	120.0	32.52	13.65
Feb. 17	23.98	100.0	7	3.00	120	120.9	30.28	12.46
Feb. 21	27.90	105.0	10	3.50	120	117.0	30.25	13.01

Data for this study were taken during two periods: DEA-solution data were taken Dec. 5-10, 1994; DEA/MDEA mixture data were taken Feb. 2-26, 1995. Data for missing days within these periods were omitted because either no data were taken, no amine concentration was recorded, the reboiler temperature was inconsistent, or the hot oil valve was 100% open.

Table 2 shows the absorber outlet conditions along with the corresponding calculated values from TSWEET.

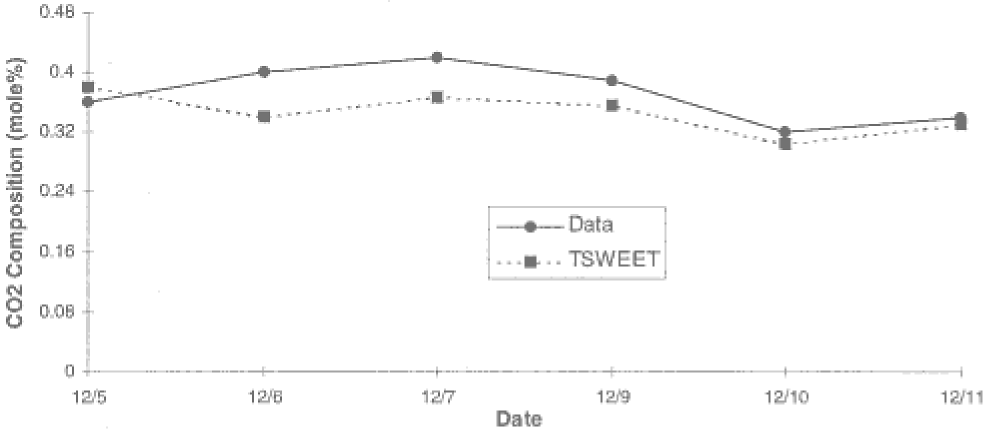
Table 2. Bryan Plant comparison of experimental results with TSWEET.

	Sweet Gas				**Rich Amine Loading mole/mole**	
	H_2S, ppm		**CO_2, %**			
Date, 1995	Data	TSWEET	Data	TSWEET	Data	TSWEET
DEA Solution						
Dec. 5	-	0.0220	0.36	0.381	N/A	0.551

Dec. 6	-	0.0220	0.40	0.341	N/A	0.543
Dec. 7	-	0.0110	0.42	0.366	N/A	0.541
Dec. 9	-	0.0630	0.39	0.355	N/A	0.557
Dec. 10	-	0.1040	0.32	0.305	N/A	0.554
Dec. 11	-	0.0910	0.34	0.331	N/A	0.554
DEA/MDEA Mixture						
Feb. 13	-	0.0130	0.10	0.100	0.396	0.430
Feb. 14	-	0.0020	<0.10	0.04	0.362	0.422
Feb. 15	-	0.0010	<0.10	0.025	0.347	0.290
Feb. 17	-	0.0006	<0.10	0.022	0.326	0.373
Feb. 21	-	0.0100	0.20	0.145	0.350	0.472

As can be seen in Table 2 and Fig. 3a, the CO_2 concentration with the DEA solution varied 0.32-0.42%. When converted to a DEA/MDEA mixture, the CO_2 concentration in the sweet gas was often less than 0.1% and never higher than 0.2% (Table 2; Fig. 3b).

Figure 3a. Sweet gas CO_2 concentration with DEA solution.



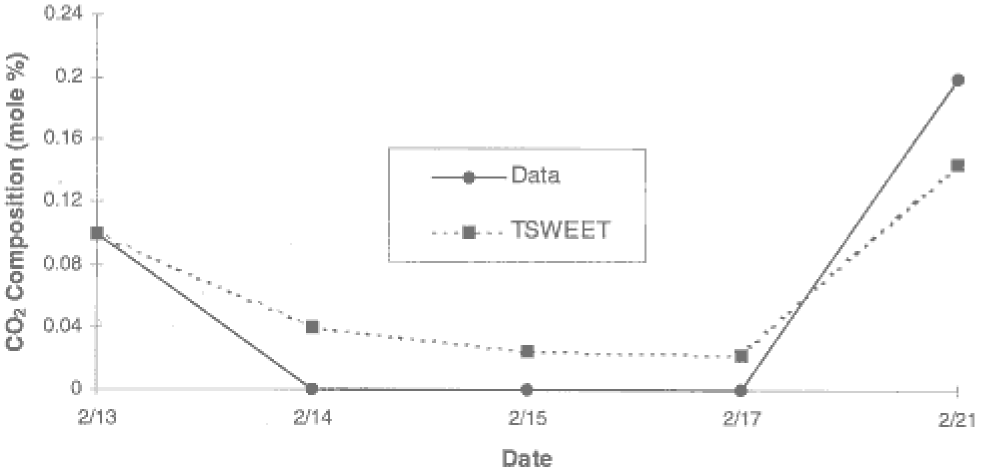


Figure 3b. Sweet gas CO_2 concentration with DEA/MDEA mixture.

As can be seen, the DEA/MDEA mixture easily produced H_2S and CO_2 concentrations less than the product specifications. The CO_2 concentration calculated by TSWEET matched the actual data very closely.

Table 2 and Fig. 4 also show the rich-amine loading (mole of acid gas/mole of amine) for the absorber with the DEA/MDEA amine mixture over time.

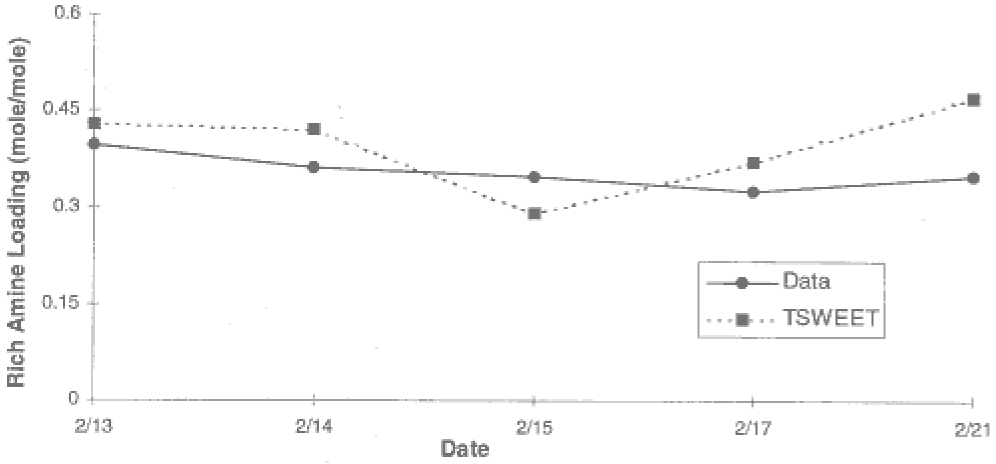


Figure 4. Rich amine loading with DEA/MDEA mix.

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