

# Design Alternatives for Sweetening LPG's and Liquid Hydrocarbons with Amines

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## ABSTRACT

Amine solutions are often used to treat LPG streams that contain acid gases. In this work, the selection of an amine and the method of contacting the amine with a 50gpm [189 lpm] LPG stream containing 7.7 mol% as CO<sub>2</sub> are evaluated. A packed contactor is compared to a static mixer and MEA, DEA, and MDEA are compared as potential solvents. A static mixer using 70 gpm [265 lpm] of 25 wt.% DEA is chosen for the final design. The operating data reveal 0.10 mol% CO<sub>2</sub> in the sweet LPG compared to the design value of 0.16 mol%.

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## INTRODUCTION

Since the inception of the gas processing industry, acid gas removal has been a very energy intensive process. The energy requirements vary depending on the acid gas concentration in the feed, the scrubbing solution concentration, the solution loading and the product purity specifications. Typical consumption ranges from about 1,000 BTU/lbm [2300 kJ/kg] to 10,000 BTU/lbm [23000 kJ/kg] of acid gas removed. The contaminants in hydrocarbon liquids and liquefied petroleum gases (LPG's) can include CO<sub>2</sub>, H<sub>2</sub>S, mercaptans, COS and elemental sulfur. In general, most liquid hydrocarbon products must meet a 1A copper strip corrosion test which corresponds to less than 4 ppm H<sub>2</sub>S. According to Perry (1977), the copper strip test is not sensitive to COS. However, in the presence of water, COS can react to form H<sub>2</sub>S. Thus liquids containing COS will often not meet the copper strip test after storage.

The most common alternatives to sweetening liquids with amines are caustic wash and molecular sieves. For significant amounts of acid gases, a caustic wash can be quite expensive due to the caustic cost and disposal problems. Molecular sieve drawbacks are large capital and operating costs as well as catalyzing the formation of COS if both H<sub>2</sub>S and CO<sub>2</sub> are present. Thus amine treatment is usually the most cost effective choice for liquid sweetening when significant amounts of acid gases are present.

In most liquid hydrocarbon or LPG production facilities, amine solutions are used to sweeten the inlet gas stream before the liquids are condensed. In these cases, amine solutions are especially convenient to use for sweetening the liquids since both absorbers can share a common amine regenerator. In this work, the design alternatives for sweetening LPGs and liquid hydrocarbons using amine solutions are discussed. An LPG sweetening unit at the Champlin Petroleum Conroe Plant was designed using the methodology presented in this work. Champlin constructed a cryogenic expander plant to remove approximately 85,000 gallons per day [322m<sup>3</sup>/day] of demethanized liquids from the Conroe Oil Field. The feed gas to the expander plant contains an average 1.68 mol% CO<sub>2</sub> and no sulfur compounds and the demethanizer bottoms product was concentrated to 7.7 mol% CO<sub>2</sub>. A CO<sub>2</sub> removal facility was required to lower the CO<sub>2</sub> concentration to below 0.16 mol%. This product was then transported by pipeline to fractionation and sales facilities near Conroe.

## ABSORBER DESIGN METHODOLOGY

The design methods available prior to 1983 for liquid-liquid acid gas absorbers were described by Honerkamp (1975). One method was to scale from an existing absorber which was not too different from the proposed new unit. However, any design faults such as massive oversizing would be transmitted to the new absorber by this method. Another method assumed a hypothetical vapor phase in equilibrium with both the liquid hydrocarbon and the amine solution as shown in Figure 1. The partial pressure of the acid gases in the hypothetical vapor was assumed to be in equilibrium with both liquid phases. This assumption is conceptually valid and should not introduce any significant error in the method. Henry's law and Raoult's Law were used to calculate the partial pressure of H<sub>2</sub>S and CO<sub>2</sub> above the hydrocarbon phase. The partial pressures of H<sub>2</sub>S and CO<sub>2</sub> above the amine solution was estimated by extrapolating the available gas phase-amine solution VLE data.

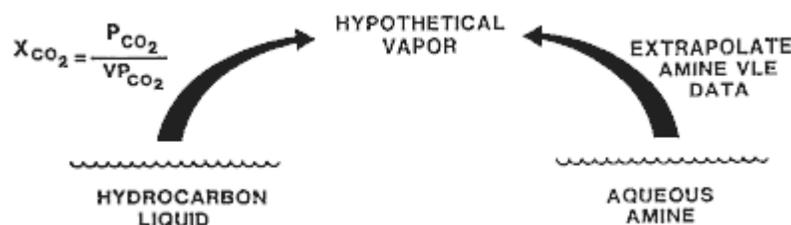


Figure 1. Amine LPG equilibria using Raoult's/Henry's Law.

A correction factor, sometimes as high as 12, was used to compensate for the non-ideal solutions, unknown activity coefficients, and extrapolated partial pressure data for amines. Since the use of empirical correction factors is risky and faulty designs are costly, a more precise method for design was needed.

In 1983, a hydrocarbon liquid sweetening capability was added to a process simulation program called TSWEET. The user supplies the operating parameters of the process and the program performs complete material and energy balances for the simulated steady-state operation. Rigorous tray-by-tray calculations are used to design the stripper and absorber columns. The liquid sweetening capability is described in Holmes et al. (1984). Again, a hypothetical vapor is assumed to be in equilibrium with both the hydrocarbon liquid and the amine solution as shown in Figure 2. The Soave-Redlich-Kwong (SRK) equation of state is used to predict the partial pressures above the LPG phase. The non-ideal solution behavior is encompassed in the SRK equation. In addition, a modified Kent and Eisenburg (1976) model is used for the amine solution and represents a very large improvement over the simple extrapolation of the H<sub>2</sub>S and CO<sub>2</sub> partial pressures. Thus, no correction factor is needed for the program results.

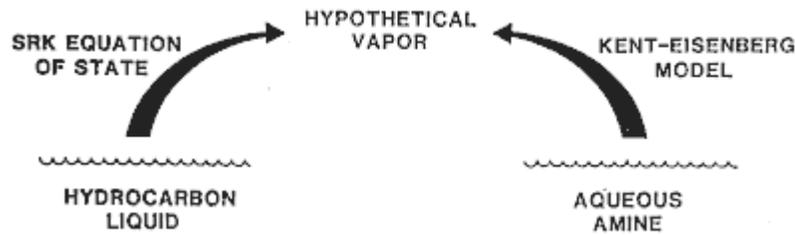


Figure 2. Amine LPG equilibria for computer simulation.

## DESIGN ALTERNATIVES

The design options for the absorber include the selection of an amine and the method of contact. Any of the commonly used ethanolamines including MEA, DEA, DGA, MDEA and the MDEA based specialty solvents will usually perform satisfactorily. The liquid-liquid contacting devices include packed towers, trayed towers, jet eductor-mixers and static mixers. Settling time for phase separation depends on the degree of turbulence in the contacting device. Typical requirements range from 10 to 30 minutes although some coalescers have been designed to reduce the separation time to as low as three minutes. As a result, the liquid-liquid contact time is sufficient for the slow  $\text{CO}_2$ -amine reaction to go essentially to completion even for the MDEA solvents which have been formulated for  $\text{CO}_2$  rejection in gas-liquid absorbers.

Based on data from several plants, Russell (1980) and Holmes et al. (1984) found that 6 ft. [1.8m] to 8 ft. [2.4m] of packed bed with a distributor plate is required for one theoretical stage in liquid-liquid contactors. Several engineers including Honerkamp (1975), Perry (1977) and Russell (1980) noted that the turndown capability for packed columns is very poor. Apparently there is insufficient data available to obtain similar guidelines for trayed columns. A typical absorber arrangement for a packed column is shown in Figure 3. Since the droplet sizes are usually not small in packed and trayed columns, the majority of the separation of the liquid phases occurs at the top and bottom of the column. A coalescer is sometimes used on the liquid product to reduce amine losses.

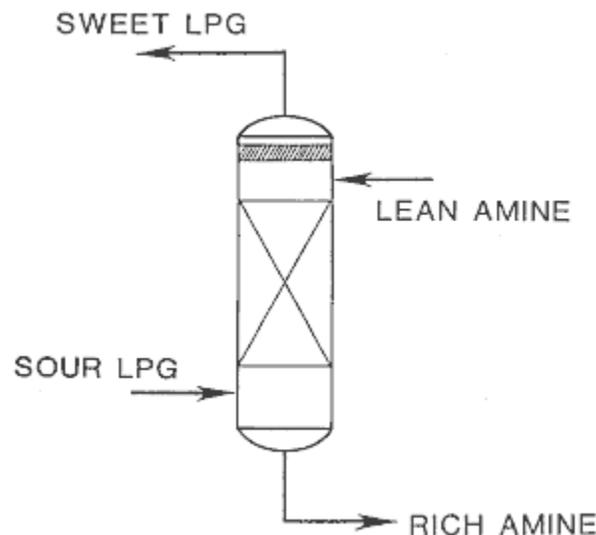


Figure 3. Typical flow diagram for liquid-liquid packed absorber.

A typical flow arrangement for static mixers or jet eductors is shown in Figure 4. The configurations of static mixers vary with manufacturers but typically contain three mixing elements at the front followed by two more near the midpoint. The length may vary from 10 diameters up to 15 ft. [4.6m]. Due to the intense mixing of the two liquid phases, 20 to 30 minutes settling times or specially designed coalescers are required to adequately separate the two phases. Based on previous work as reported in Holmes et al. (1984) and some additional plant data, the acid gas removal efficiency of a mixer-separator combination ranges from 95% to 98% of one ideal

stage. If a single contactor-separator will not produce specification product, a second contactor-separator arrangement may be added as shown in Figure 5. If the rich amine from the second contactor-separator is not heavily loaded, it may be used as feed to the first contactor. The rich amine from the first contactor must be separated from the hydrocarbon liquid and fresh lean amine must be fed to the second contactor to achieve efficiencies greater than one ideal stage. If a second contactor-separator is required, the intermediate liquid-liquid separator may be reduced in size since complete separation is not necessary.

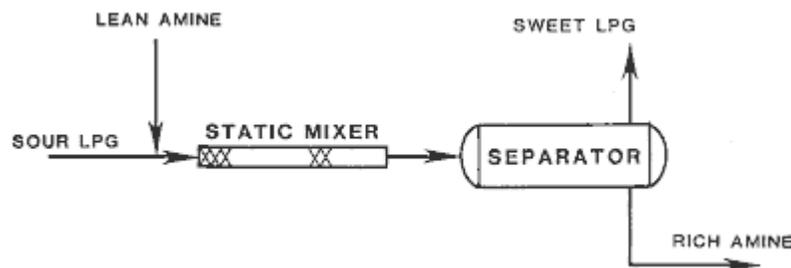


Figure 4. Typical flow diagram for single stage static mixer.

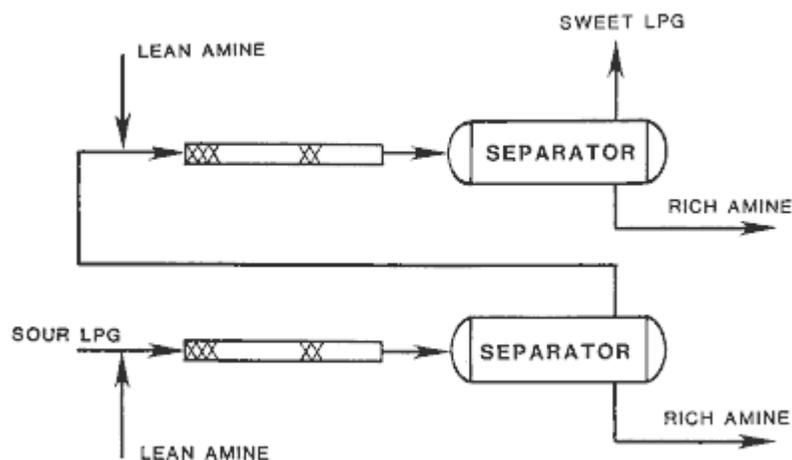


Figure 5. Typical flow diagram for two stage static mixer.

## APPLICATION OF DESIGN ALTERNATIVES

A design procedure for liquid sweetening units using amines follows:

1. Select an amine to use. Use a slip stream of lean amine if it is available from an existing unit. Otherwise, DEA is usually the best choice.
2. Perform stage calculations for the absorber using a process simulation program. In most liquid sweetening applications, a single ideal stage is sufficient to meet required purity specifications.
3. Determine absorber equipment design alternative which is the most economically suitable. The guidelines are six to eight feet [1.8 to 2.4m] of packing per ideal stage for packed columns and a separation efficiency of 95 to 98% of one ideal stage for static mixers and jet eductors. The outlet concentration for static mixers or jet eductors is:

$$\text{Outlet Conc.} = \text{Inlet Conc.} - \text{Stage eff. } (\Delta C)$$

$$\Delta C = (\text{Inlet Conc.} - \text{Predicted* Conc.})$$

\* For one ideal stage

If a second static mixer is used, the outlet from the first stage is the feed to the second stage.

These guidelines were used to explore the design alternatives for a unit to treat the Champlin demethanizer bottoms product stream shown in Table 1. The stream contained 7.7 mol % CO<sub>2</sub> and had to meet a 0.16 mol% specification before entering the pipeline.

Component	Mol %
CO <sub>2</sub>	7.70
C1	0.58
C2	44.25
C3	21.81
C4	12.89
C5	6.77
C6+	5.99
Temperature = 56F [13.3C] Pressure = 780 psig [53.8 bar] Flowrate = 50 gpm [189 lpm]	

In this application, MEA, DEA and MDEA are compared as potential solvents and a packed column is compared with a static mixer for contacting the liquids. The TSWEET simulation program performed the calculations for the various alternatives.

*Packed Contactor* -- The results from the analysis of a packed column representing one ideal stage are shown in Table 2. Due to the increased molar concentration of amines, lower amine flowrates are required to produce specification product with DEA and MDEA. This is most apparent when comparing the 25 and 33 wt. % DEA cases. For the 33 wt. % DEA case, the primary savings would result from a substantially smaller regeneration unit and reboiler duty. However, the absorber would be only moderately smaller since the LPG flowrate of 50 gpm [189lpm] strongly influences the absorber diameter.

	MEA	DEA	DEA	MDEA
Wt. % Amine	15.0	25.0	33.0	50.0
Flowrate (gpm)[lpm]	45.0[170]	44.0[167]	33.5[127]	41.0[155]
Lean Loading (mol/mol)	0.12	0.03	0.03	0.01
Rich Loading (mol/mol)	0.54	0.40	0.43	0.27
CO <sub>2</sub> out (%)	0.15	0.15	0.15	0.15
Absorber Dia. (in.)[cm]	34[86]	34[86]	32[81]	34[86]
Duty (MMBtu/hr)[MW]	2.90[0.85]	2.32[0.68]	1.76[0.52]	2.15[0.63]

Absorber equipment consists of a column with an eight foot [2.4m] packed section and sufficient space above and below the packing to separate the LPG and aqueous phases. As a result, the absorber would have an I.D. of 32 in. [81cm] to 34" [86cm] and an approximate height of 20 ft. [6.1m]. A final coalescer also could help reduce amine losses in the LPG stream. Level controllers on the absorber and coalescer maintain the interface at the top or bottom to obtain optimum performance.

*Static Mixer Contactor* -- Operating data from previous plants with static mixers show that the acid gas removal efficiency of a static mixer/coalescer combination commonly ranges from 95 to 98% of one ideal stage. A major factor contributing to the efficiency is the relative flowrates of the amine solution and the hydrocarbon stream. A higher ratio of amine flow to hydrocarbon flow leads to better efficiency.

A detailed analysis of a static mixer to treat the LPG in Table 1 was performed. Table 3 compares the performance of MEA, DEA and MDEA, assuming the static mixer to have an efficiency of 98.2% of an ideal stage. With all three amines, the CO<sub>2</sub> outlet concentration decreases with increased amine solution flowrate until a

plateau is reached. This trend is shown graphically in Figure 6 for 25 wt. % DEA. Thus, a 98.2% efficiency is required to produce the 0.16 mol% CO<sub>2</sub> specification when using 70 gpm [265lpm] of 25 wt. % DEA to scrub the LPG. On the basis of the results shown in Table 3, a somewhat smaller flowrate would be required for 15 wt. % MEA and for 33 wt. % DEA. However, the flowrate required for MDEA would have to be approximately 50% higher.

	MEA	DEA	DEA	MDEA	PLANT DATA
Wt. % Amine	15.0	25.0	33.0	50.0	25+
Flowrate (gpm)[lpm]	60.0[227]	70.0[265]	60.0[227]	120.0[454]	70.0[265]
Lean Loading (mol/mol)	0.12	0.03	0.03	0.01	-
Rich Loading (mol/mol)	0.436	0.303	0.256	0.10	-
Efficiency (%)	98.2	98.2	98.2	98.2	98.7
CO <sub>2</sub> out (%)	0.16	0.16	0.16	0.16	0.10

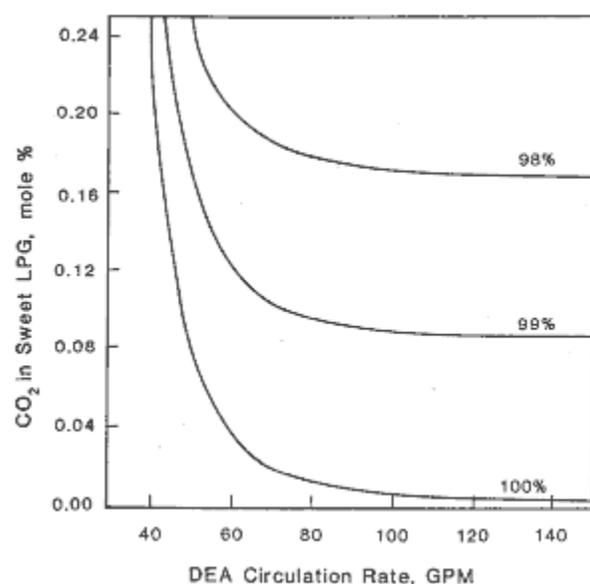


Figure 6. Performance of a static mixer with 25 wt. % DEA at various stage efficiencies.

On the basis of these calculations for the static mixer and other process considerations, the plant engineers selected a static mixer/coalescer design using 70 gpm [265lpm] of 25 wt. % DEA to scrub the LPG. The coalescer had a residence time of about 3.5 minutes based on the combined amine and LPG streams. The operating results from the unit are also shown in Table 3. Based on the measured concentration of 0.10 mol% CO<sub>2</sub> in the outlet, the static mixer efficiency was 98.7%. This excellent efficiency is believed to be due to the relatively large volume (70 gpm [265lpm]) of amine solution used to scrub the 50 gpm [189lpm] LPG. Some efficiency improvement could have been realized from the internal design of the coalescer.

## SUMMARY

The absorber design alternatives for sweetening hydrocarbon liquids using ethanolamines were explored with the aid of the process simulation program TSWEET. The most common liquid-liquid absorbers are packed towers, jet eductor-mixers and static mixers. The design guidelines of six to eight feet [1.8 to 2.4m] of packing per ideal stage for packed columns and 95% to 98% separation efficiency for mixers were used to explore alternatives to sweeten a 50 gpm [189lpm] LPG stream with 7.7 mol % CO<sub>2</sub>. For this application, MEA, DEA, and MDEA were considered as potential solvents in a packed column and in a static mixer/coalescer. A static mixer arrangement

using 70 gpm [265lpm] of 25 wt. % DEA was selected for the design. The operating data revealed 0.10 mol% CO<sub>2</sub> in the sweet LPG as compared to the design value of 0.16 mol%.

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