Sweetening LPG's with Amines

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ABSTRACT

As more LPG's (liquefied petroleum gas) are being produced, the demand for liquid hydrocarbon sweetening facilities has increased. The most common contaminants in LPG's are CO2, H2S, mercaptans, COS, CS2, and elemental sulfur. Each of these contaminants can cause problems in the finished products.

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Introduction

As more LPG's (liquefied petroleum gas) are being produced, the demand for liquid hydrocarbon sweetening facilities has increased. The most common contaminants in LPG's are CO_2, H_2S, mercaptans, COS, CS_2 and elemental sulfur. Each of these contaminants can cause problems in the finished products.

H_2S is corrosive and its presence can lead to deposition of free sulfur. Although mercaptans are used in small quantities for odorizing products, in larger quantities they impart a bad odor to the product as well as the combustion flue gases. According to Perry (1), COS does not react to copper strip tests. However, the COS can hydrolyze to H_2S which can cause a product with no H_2S to become sour after setting in a tank. Thus, if both COS and water are present in a product, removal of COS must be considered. The presence of CO_2 in LPG's can also cause problems. For example, if the product is treated with caustic, the presence of CO_2 can cause large caustic losses.

Historically, several methods have been used to remove the contaminants. If the quantities of the contaminants are small, a simple caustic wash can be used. For larger quantities molecular sieves and amine treating systems can be used. While molecular sieves have the advantage of removing water and COS along with H_2S and CO_2, their disadvantages include large capital and operating cost as well as catalyzing the formation of COS when both H_2S and CO_2 are present.

The use of amines has become quite popular, especially in plants where amines are also being used to sweeten the gas stream before processing for the LPG's, Figure 1. In plants with multiple absorbers, a common stripper can be used to regenerate the amine. Although several LPG sweetening units using amines are currently in use,

many aspects of the design of these plants have been more of an art than a science. For the most part, the designs have involved approximations based on existing plants and guesswork.

Figure 1.
Common sweetening plant.
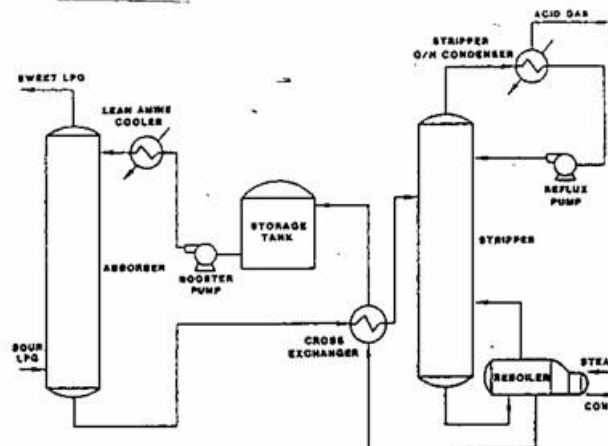
This article discusses the design methods for LPG sweetening units using amines and recent design advances in process simulation. The results from the process simulation program for LPG sweetening are compared to data from operating plants.

Design methodology

Based on the operating experience for LPG sweetening plants using MEA (monoethanolamine), DEA (diethanolamine), and DGA, (1-5) the recommendations in Table 1 were made for design guidelines for the various amines. All of the amines are degraded to some extent by COS and CO_2. However, DEA is degraded less than MEA. In addition, less reboiler heat is required for DEA due to higher solution concentrations and loading as well as lower heats of absorption. Excessive corrosion could be encountered if the recommended loadings are exceeded.

Table 1.
Operating conditions for LPG sweetening with amines

| Amine	Wt. % Amine	Max Loading mol/ mol*
MEA	5-20	0.3 - 0.4
DEA	25-35	0.35 – 0.65
DGA	50-70	- -

* Mol acid gas per mol amine.

Current Methods.

As pointed out by Honerkamp (4), two approaches have been generally used to determine necessary amine circulation rates and types of contact surface required. One is to ratio up or down from an existing plant not too different from the proposed new one. The other is to extrapolate available gas-amine data into the expected operating range.

The scale-up or -down procedure is very straightforward and needs no further explanation. Obviously, any problems with the existing plant such as massive oversizing will be transmitted to the new unit.

In the extrapolation method, a hypothetical vapor phase is assumed to be in equilibrium with both the LPG and

the amine solution, Figure 2. Henry's law and Raoult's law are used to calculate the partial pressure of the H_2S and CO_2 above the LPG. Using these laws for CO_2 as an example, the concentration of CO_2 in the LPG is the partial pressure of the CO_2 in equilibrium with the LPG divided by the vapor pressure of pure CO_2 at the same temperature. The partial pressure of the CO_2 in the hypothetical vapor phase is assumed to be the equilibrium partial pressure of the CO_2 above the amine solution. A correction or safety factor of up to a factor of 12 is then applied to the equilibrium partial pressure. The correction factor is used to compensate for the nonideal solutions, unknown activity coefficients, and extrapolated partial pressure data for amines.
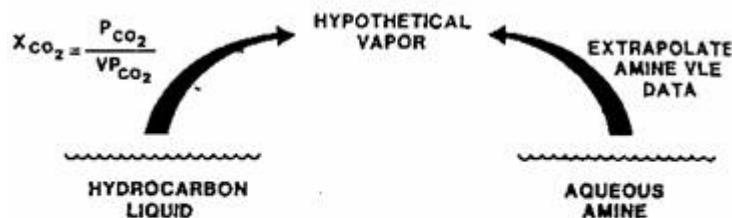
Figure 2. Amine LPG equilibria using Raoult's/Henry's law.

Based on this method, the calculated equilibrium partial pressure of CO_2 above the amine is so far below the CO_2 partial pressure above the LPG that equilibrium considerations are not important. The only exceptions would be for very small CO_2 concentrations in the inlet or for very high amine loadings. In addition to the equilibrium considerations, the lean amine should be regenerated to less than 0.1 mol/mol. Heretofore, only correlations have been available to estimate the performance of the still and the lean amine concentrations.

Computer Simulation.

The design capability of LPG sweetening plants using amines has been greatly advanced with the expanded capabilities of a process simulation program called Tsweet. This program was originally written for gas sweetening plants using amines and has now been expanded to include LPG streams.

Tsweet is an advanced process simulation program using the flexible flowsheet concept. Beginning with the process flowsheet and operating parameters, complete material and energy balances for the steady-state operating conditions can be performed. Rigorous tray-by-tray calculations using the Ishii-Otto (6) method are used to predict the design of the stripper and absorber columns. Some 24 chemical species are allowed, including MEA, DEA, DGA, MDEA, water, H_2S CO_2 and an assortment of gases commonly present in natural and synthetic gases. Vapor pressures of H_2S and CO_2 over the amine solutions are calculated by a modified Kent and Eisenburg (7) equilibrium-model. A kinetic model was developed to predict the effect of residence time, temperature, solution concentration, pressure and type of amine on the rate of CO_2 absorption.

The program has been demonstrated to be very reliable in calculating the performance of amine gas sweetening plants. The program will accommodate multiple absorbers in LPG and/or gas service which feed a common stripper. The gas sweetening capabilities of Tsweet have been described by Polasek et al. (8) and Bullin and Polasek (9).

To facilitate LPG sweetening in the program, the hypothetical vapor phase discussed was used. The hypothetical vapor is assumed to be in equilibrium with both the LPG and amine solution, Figure 3. The Soave-Redlich-Kwong (SRK) equation of state was used to predict the partial pressures above the LPG phase. The nonideal solution behavior is encompassed in the SRK equation. In addition, the theoretically-based Kent and Eisenburg model for the amine solutions represents a very large improvement over a simple extrapolation of the H_2S and CO_2 partial pressure. Thus, no correction factor should be needed for the program results.
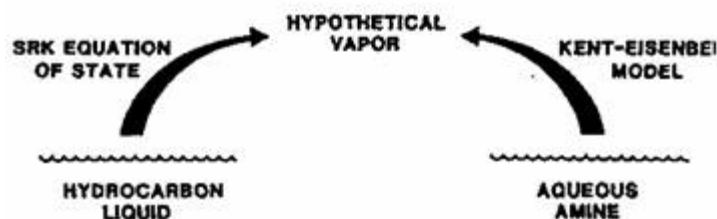
Figure 3.Amine LPG equilibria for computer simulation.

Tsweet results vs. plant data

The new simulation capability for LPG sweetening plants using amines is compared to data from several plants involving a wide variety of contactors. The types of contactors include packed columns, sieve tray columns, jet eductor mixers, and static mixers. According to Russell (5), about 6 to 8 ft (1.83 to 2.44 m) of packed bed with a distributor plate is required for one theoretical stage in liquid-liquid contactors. Honerkamp(4), Perry (1), and Russell (5) have noted that the separation efficiency for a packed column is significantly reduced at high turndown. Depending on the degree of turbulence in the contactor settling retention times from 10 to 30 minutes is required for good phase separation.

Tsweet is compared to operating data from eight plants, Table 2. The operating data for plants 1 through 7 were reported by Honerkamp(4). The comparisons are discussed on an individual plant basis below.

Plant 1.

The absorber for this plant was a 30 in. (0.76 m) diameter column with three 12 ft (3.66 m) sections of 1 in. (2.54 cm) Intalox packing. Thus, three ideal stages were used for the simulation results, Table 2. The outlet CO_2 of 0.056 ppm calculated by Tsweet was close to the zero value reported in the data. The program was also run for one and two ideal stages. The calculated outlet CO_2 was 18.7 and 0.058 ppm, respectively. Thus, the absorber was severely oversized. The stripper calculations also matched the data well as shown by the lean solution loading.

Table 2.
Tsweet results vs, data for LPG sweetening with amines.

		1		2		3	
Case	Data	TSweet	Data	TSweet	Data	TSweet
Hydrocarbon Rate, gpm	100	103	780	780	208	210
T, ºF	50 – 60	55	90	90	77 -89	83
P, psig	500	500	535	535	835	835
CO_2 in, ppm	10,000	10,000	2,030	2,023	33,000	33,000
H_2S in, ppm	--	--	Trace	2.7	--	--
CO_2 out, ppm	0	0.056	< 100	0.42	Trace	0.4
H_2S out, ppm	--	--	--	0.01	--	--
Amine	MEA	MEA	MEA	MEA	MEA	MEA
Wt. %	20	20	15	15	20	20
Flow, gal/min	10.8	10	34	34	54	50
Ideal Stages **	--	3	--	2	--	2
Lean Loading *	0.10	0.108	0.10	0.13	0.10	0.11
Rich Loading *	0.44	0.44	0.28	0.32	0.53	0.53
Contactor	Three 12 ft. sections of packing		Two 12 ft. sections of packing		18 ft. of packing	

Table 2.
Tsweet results vs, data for LPG sweetening with amines (continued).

Case	4 Data	4 TSweet	5 Data	5 TSweet	6 Data	6 TSweet
Hydrocarbon Rate, gpm	265	273	42	44	21	22
T, ºF	--	80	80 - 90	85	--	85
P, psig	305	305	--	200	265	265
CO_2 in, ppm	2,460	2,450	5,000	5,020	nil	--
H_2S in, ppm	270	270	--	--	1,080	1,080
CO_2 out, ppm	Trace	1.2	100	47	--	--
H_2S out, ppm	nil	5.9	--	--	nil	9.2
Amine	DEA	DEA	MEA	MEA	MEA	MEA
Wt. %	20	20	8	8	5	5
Flow, gal/min	20	20	5.3	5.3	< p align=center>5	5
Ideal Stages **	--	2	--	1	--	1
Lean Loading *	0.07	0.05	0.10	0.10	0.07	0.07
Rich Loading *	0.30	0.27	0.44	0.43	0.13	0.13
Contactor	Two 8 ft. sections of packing		10 perforated trays		Jet eductor-mixer	

Table 2.
Tsweet results vs, data for LPG sweetening with amines (continued).

Case	7 Normal Data	7 Normal TSweet	7 Maximum Data	7 Maximum TSweet	8 Data	8 TSweet
Hydrocarbon Rate, gpm	250	250	200	205	105	105
T, ºF	55	55	55	55	100	100
P, psig	435	435	435	435	385	385
CO_2 in, ppm	2,260	2,200	6,675	6,630	7,260	7,260
H_2S in, ppm	--	--	--	--	--	--
CO_2 out, ppm	nil	0.90	138	74	660	158
H_2S out, ppm	--	--	--	--	--	--
Amine	MEA	MEA	MEA	MEA	DEA	DEA
Wt. %	15	15	15	15	30	27
Flow, gal/min	100	110	100	93	14	14
Ideal Stages **	--	1	--	1	--	1
Lean Loading *	0.20	0.20	0.38	0.38	0.30	0.30
Rich Loading *	0.22	0.22	0.46	0.45	0.25	0.32
Contactor	Jet eductor-mixer		Jet eductor-mixer		Static mixer	

* Loadings are moi of acid gas per mol of amine. A lean solution loading of 0.1 mol/moi was assumed if no information was available.

** Equilibrium stages used in the absorber.

SI Conversion: kPa » psi X 6.89; L - gal X 3.79; m - ft X 0.3048; °C - (°F - 32)/1.8.

Plant 2.

A vertical column absorber with two 12 ft (3.66 m) sections of packing was used. Two ideal stages were used for the Tsweet results, Table 2. Since a trace of H_2S in the inlet was reported, an H_2S feed rate of 0.01 lb mol/h (4.54 gmol/h) which corresponds to 2.7 ppm was assumed for Tsweet. For this inlet rate, 0.01 ppm H_2S was calculated for the sweet LPG. The calculated CO_2 was 0.42 ppm compared to the reported value of less than 100 ppm. Plant 2 was also simulated using one ideal stage. The outlet concentrations were 4.2 ppm CO_2 and 0.24 ppm H_2S. Thus, one 12-ft (3.66-m) section of packing would have been adequate to meet the plant requirements.

Plant 3.

A 48 in. (1.22 m) diameter absorber with 18 ft (5.49 m) of packing was used in Plant 3. The inlet CO_2 was 3.3 mol % and the outlet was reported as a trace. For one and two ideal stages, the program results were 848 and 0,4ppmCO_2out, respectively. The 18 ft (5.49 m) of packing with only one distributor probably represented between one and two ideal stages. Thus, one ideal stage would not be adequate for this plant.

Plant 4.

In this case, a 66 in. (1.68 m) diameter absorber with two 8 ft (2.44 m) sections of ceramic packing was used. The design hydrocarbon rate was 525 gal/min (1,987 L/min) compared to the actual rate of 265 gal/min (1,003 L/min). DEA was used as the amine. For two ideal stages, the outlet H_2S was about 5 ppm compared to the trace reported in the data. Since no inlet LPG temperature was reported in the data, a value of 60°F (15.6°C) was also used in Tsweet in an effort to match the data. The outlet H_2S dropped to only about 4 ppm. In another effort to match the data, the lean amine concentration was lowered to 0.04 mol/mol. However, the outlet H_2S fell only to 2.9 ppm. Since a value of "nil" was reported for H_2S, a copper strip corrosion test was probably used.

According to Perry (7), a 1A copper strip is generally thought to represent H_2S concentrations below about 1 to 2 ppm. Baumer(3) suggested that a 1A copper strip can be obtained at H_2S levels as high as 3 or 4 ppm. The only other potential explanation for the plant's performing better than the program calculation for two ideal stages was that the two 8 ft (2.44 m) packed sections performed better than two ideal stages. However, three ideal stages along with the other conditions shown in Table 2 resulted in an outlet H_2S of 3.2 ppm. Thus, the plant appears to be performing better than equilibrium.

Plant 5.

A 30 in. (0.76 m) diameter absorber with ten perforated trays was used. The design LPG rate was 85 gal/min (322 L/min) compared to the operating rate of 42 gal/min (159 L/min). The calculated value for the 42 gal/min (159 L/min) case using one ideal stage was 47 ppm compared to the 100 ppm data value. The fact that liquid-liquid contactors lose efficiency rapidly with turndown is well known. When the contactor was operated at the design rate of 85 gal/min (322 L/min), the outlet CO_2 was 50 ppm. For one and two ideal stages for the 85 gal/min (322 L/min) case, the program values were 1,130 and 540 ppm for the outlet CO_2 and 0.601 and 0.677 mol/mol for the rich amine loading, respectively. In both cases the rich amine was loaded to 100% of equilibrium. Thus, the amine flow must have been increased when the 85 gal/min (322 L/min) data were taken.

Plant 6.

The contactor for this plant was a jet eductor-mixer. The eductor was followed by a settling tank with a residence time of about 30 min. Very little CO_2 was present in the feed while the H_2S was about 1,080 ppm. The calculated values for the outlet H_2S were 9.2 and 2.9 ppm for one and two ideal stages, respectively. The reported concentration was "nil." Unless two or more jet eductors are used, more than one ideal stage is not possible. In fact, a single jet eductor seldom performs as one full ideal stage. No additional information was available on this

plant Thus, the differences between the data and the program could not be explored further.

Plant 7.

A jet eductor-mixer and settling tank combination was also used for Plant 7. Most of the rich amine stream was recycled directly back to the eductor. A slip stream was regenerated and returned to the eductor. This plant was operated at two levels of CO_2 in the feed corresponding to the "normal" of 2,260 and the "maximum" of 6,675 ppm. For the normal CO_2 content, the program calculated an outlet CO_2 of 0.9 ppm compared to the data value of "nil." For the maximum CO_2 content, the program predicted 74 ppm compared to 138 ppm. The amine circulation rates were kept constant at 15 gal/min (56.8 L/min) for both cases. However, the LPG rate was decreased from 250 gal/min (946 L/min) for the normal case to 200 gal/min (757 L/min) for the maximum case. As expected, the jet eductor is probably not acting as a full ideal stage.

Plant 8.

A static mixer consisting of five mixing elements was used to contact the LPG and DEA solution. The static mixer was 3 in. (7.62 cm) in diameter with an overall length of 15 ft (4.57 m). The mixing elements were grouped 3 at the inlet and 2 near the middle of the mixer. Each element was 3 in. (7.62 cm) long and reversed the direction of the swirl. The contactor was followed by a separator and a final coalescer. The CO_2 content of the sweet LPG was 660 ppm. Using one ideal stage, the program predicted 158 ppm CO_2, The performance of the static mixer system was excellent to approach an ideal stage this closely.

In summary

The previous design methods for LPG sweetening plants using amines were based on either a simple scale-up or -down from an existing plant or an extrapolation of gas-amine information. The extrapolation method requires a correction factor of up to a value of 12. Another method based on computer simulation has become available. The capabilities of the amine-gas sweetening program, Tsweet, were expanded to handle LPG streams. The program uses the SRK equation of state for the LPG and modified Kent and Eisenburg model for the amine solutions. The entire plant including the stripper is solved by Tsweet.

Results from the program were compared to data from eight plants with a wide variety of contactors including packed columns, perforated plate columns, jet eductor-mixer, and static mixers. The predicted values from Tsweet matched the data quite well except for the one plant with a jet eductor.

Tsweet was also used to examine the extent of contact needed in the various plants. Based on the program and the data from eight plants, one ideal stage is sufficient to remove the CO_2 up to about 0.5% for most applications using MEA.

REFERENCES

1. Perry, C. R., Oil and Gas J., p. 76 (May, 1977).

2. Bacon, K. H., "Liquid Treating," Warren Petroleum Co., Tulsa, Ok.

3. Baumer, J. A., "Large Scale Liquid-Liquid DEA Treating for Fractionation Plants," Regional GPA Meeting, Houston (Nov., 1981).

4. Honerkamp, J. D., **Treating Hydrocarbon Liquids with Amine Solutions," Proc. Gas Conditioning Conf. (1975).

5. Russell, R. M., Oil and Can «/., p. 1.15 (Dec., 1980).

6. Ishii, Y., and F. D. Otto, Can J. of Chem. £/#.. 51, p. 601 (Oct., 1973).

7. Kent, R. L., and B. Eisenburg. Hydro. Proc., p. 87 (Feb., 1976).

8. Polasek, J. C., S. T. Donnelly, and J. A. Bullin, Chem. Eng. Prog., p. 63 (Mar., 1983).

9.- Bullin J. A., and J. C. Polasek, "Selective Absorption with Amines," Proc. 6lst Annual Gas Processor's Com;. (1982).