Dome's North Caroline Plant Successful Conversion to MDEA

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ABSTRACT

Canada's first plant conversion from DEA to MDEA is a success. Dome's North Caroline amine plant performs very smoothly after being debottlenecked to, at least, original design capacity. Performance data taken for the absorber at several amine flow rates compare with safe accuracy to values calculated by the TSWEET program that was used as the basis for conversion.

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"Simulation values prove out in DEA to MDEA switch" Oil & Gas Journal August 6, 1984: 47-50.
"Switch to MDEA raises capacity" Hydrocarbon Processing May 1984: 79-82.

INTRODUCTION

The North Caroline Plant was built in 1980 and was designed to operate primarily unattended with operators present at the plant only eight hours a day. As shown in Fig. 1, the feed gas, from a gathering system, passes through a standard refrigeration plant where liquids are extracted and then flows through an amine unit for sweetening to pipeline specifications (2% CO_2, 1/4 grains H_2S/100 SCF).

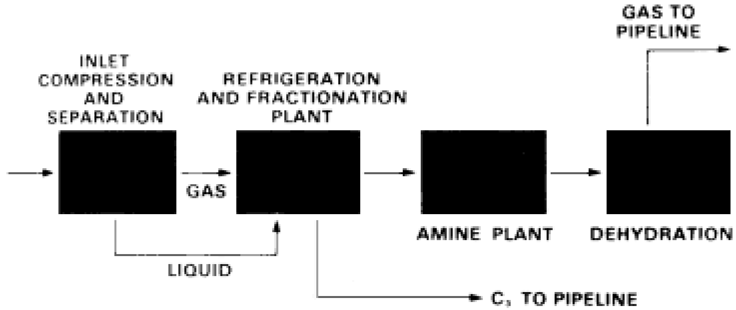

Fig. 1. North Caroline Plant Schematic

The amine unit, Fig. 2, was designed to process 47 MMSCFD of gas containing 2.65% CO_2 and 100 PPM H_2S. The amine solution concentration was 33% per weight of diethanolamine (DEA). The absorber contained 21 valve trays. After the plant was built, several new wells were completed and brought onstream. However, these new wells increased the CO_2 concentration in the amine unit feed to about 3.5%. The H_2S remained relatively constant at about 50 PPM. The amine unit could not accommodate this large increase in CO_2. As a result, the capacity of the whole plant was reduced to 35.0 MMSCFD. At this gas flow, the rich amine loading was 0.48 mole acid gas/mole amine. The amine unit thus became the bottleneck of the entire plant at North Caroline.

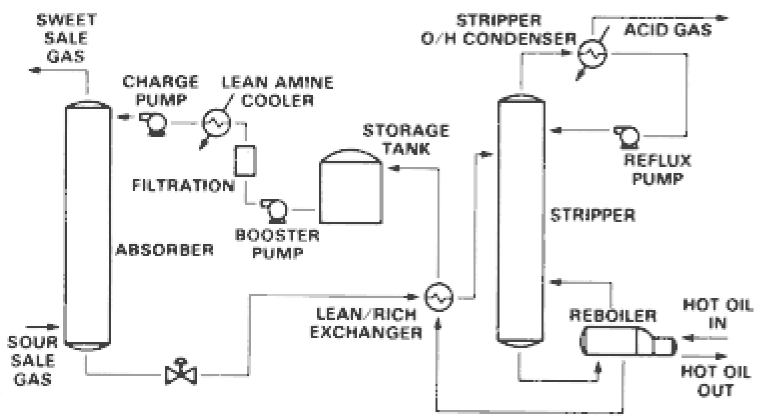

Fig. 2. Process Schematic for North Caroline Sweetening Plant

In addition to the capacity reduction, the amine unit operation became unstable, because the stripper was working at its utmost limit, close to the shutdown point. Thus, any upset would bring the plant down. Furthermore, it produced gas only marginally below the 1/4 gr H_2S /100 SCF specification. The H_2S came primarily from one well which was usually around 300 PPM. However, each time this well was shut-in for a few hours, the H_2S from the well increased to about 1200 PPM for a short period after start-up. Since the amine unit could not tolerate any additional H_2S, the H_2S peak from the well caused the sales gas to exceed pipeline specifications and the sales gas would be automatically flared.

Due to a need for increased capacity, Dome decided to debottleneck the plant to its original capacity as well as to stabilize the plant operation. The following three alternatives were available for debottlenecking the plant:

1. Build a complete parallel amine system to process 12 MMSCFD.
2. Attempt to increase the loading of the DEA in the existing unit to 0.65 mole/mole.
3. Convert the amine unit from DEA to Methyldiethanolamine (MDEA).

The first alternative was obviously very expensive. The second alternative would require a major revamping of the amine plant and heating system because the stripping column and reboiler would be undersized. In the third alternative, if MDEA could slip a significant portion of the CO_2 through the absorber and into the sales gas, the existing facility would probably have sufficient capacity to process 47 MMSCFD which was the original design rate. Thus based on cost considerations, the MDEA alternative warranted further investigation.

MDEA has several distinct advantages over primary and secondary amines. These include lower vapor pressure, higher resistance to degradation, fewer corrosion problems, lower heat of reaction, and, most importantly, selectivity toward H_2S in the presence of CO_2. Most of the above advantages have also been reported by Blanc et al.[2] The enhanced selectivity of MDEA for H_2S 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. At least six different mechanisms for the CO_2-MDEA reaction have been proposed by Cornelissen,[4] Barth et al,[1] and Danckwerts.[5] MDEA can react with H_2S by the same proton transfer mechanism of primary and secondary amines (Jou et al.[8]). Selective absorption of H_2S results from optimizing the absorber design and the circulation rate to give residence times and reactor conditions favorable to H_2S absorption into the amine solution and to CO_2 retention in the sales gas.

Three sources of MDEA technology were investigated by Dome. The first source was from a licensor who recommended changes to the lean/rich exchanger to save energy, the addition of nozzles to the absorber and the addition of a heater on the gas at the inlet of the absorber. The second source was from another licensor who recommended the extension of the still height to accommodate eight additional trays, structural reinforcement of the still and the addition of two nozzles to the absorber.

The third source of MDEA technology was from a process simulation program for amine sweetening units, called TSWEET. This program was developed by Bryan Research and Engineering, Inc. and 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 steady state operating conditions can be performed. Rigorous tray-by-tray calculations using the Ishii-Otto[7] method are used to predict the design of the stripper and absorber columns. Vapor pressures of H_2S and CO_2 over the amine solutions are calculated by a modified Kent and Eisenberg[9] 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 demonstrated to be very reliable in calculating the performance of amine gas sweetening plants. The gas sweetening capabilities of TSWEET have been previously described by Polasek et al,[10] Holmes et al,[6] and Bullin and Polasek.[3]

Based on the TSWEET program results for the North Caroline plant, Dome concluded that MDEA could do the job. TSWEET also showed that the existing equipment had sufficient capacity and that no equipment modifications were necessary. Thus, Dome decided to convert the plant to MDEA using Dome’s engineering group in collaboration with Propak Systems Ltd., and with Bryan Research and Engineering providing support on the use of TSWEET.

PLANT SHUTDOWN AND STARTUP

As a result of the decision to convert to MDEA without mechanical modifications, the North Caroline plant was shut down and the DEA was drained from the amine sweetening unit. The equipment was cleaned with three separate washes The first was with 9% sulfamic acid combined with 1% citric acid and about 6% degreaser, the second wash was with 5% soda ash and the last wash was with 2% MDEA in water. The MDEA was added in the last wash in order to eliminate any compounds present in the equipment which could have reacted during operation with MDEA and modified its properties. The amine plant was then charged with 33 wt% MDEA and started up. The plant was allowed to operate for three or four days before the testing was initiated. The start up was very smooth and no significant problems were encountered.

TESTING AND ANALYTICAL PROCEDURES

The absorber performance at the North Caroline plant was studied as a function of the amine flow rate to the absorber. At each amine flow rate, data was taken on gas flow, composition, temperature and pressure of the feed and exit gas; composition, flow and temperature of the lean amine; rich amine temperature and five temperatures down the absorber. All flow rates were measured by orifice meters and all temperatures were measured by calibrated thermocouples. The gas compositions were determined by gas chromatography. The acid gas concentrations in the lean amine were determined by titrametric methods. For H_2S, the amine solution was added to an excess of acidified iodine solution and back titrated with sodium thiosulphate. Thus, the method yielded the total H_2S including thiosulphate and any other substances that consume iodine The CO_2 in the amine solution was precipitated with excess barium chloride and the CO_2 was determined by acid titration.

PLANT PERFORMANCE, PLANT TESTS COMPARISON TO TSWEET

After switching to MDEA, the North Caroline amine unit was operated without problem. Contrary to the operation with DEA, the H_2S concentration in the sales gas has never been near 1/4 gr/100 SCF and, in fact, it has been less than 0.06 gr/100 SCF. The operation with MDEA has been far more stable and there have been no spurious shutdowns. Presently, when the high H_2S well is put on-stream, no special precautions are taken to prevent plant shutdown and consequential flaring of the sales gas due to high H_2S content. As a matter of fact, the operator cannot tell whether the high H_2S well is on stream or not. The amine plant has now been debottlenecked to its initial capacity and possibly higher.

Table I
North Caroline Plant MDEA Modifications
Inlet Conditions to the Absorber

	INLET GAS				LEAN AMINE				
Test	Flow MMSCFH	Temp ^oF	H_2S Conc. PPM	CO_2 Conc. %	Flow GPM	Temp ^oF	WT%	H_2S gr/gal	CO_2 gr/gal
1	1.29	84	50	3.52	69.6	97	33.0	1.00	50.1
2	1.30	85	58	3.47	83.5	100	33.0	1.00	54.0
3	1.30	90	56	3.47	99.8	111	33.0	0.50	42.4
4	1.23	92	58	3.47	116	115	33.0	1.49	45.0
5	1.26	92	55	3.48	123	120	33.1	0.50	57.8

The plant tests were initiated about three days after start up with MDEA. The primary series of tests involved the reduction of the amine flow rate in steps from 123 gpm to 69.6 gpm. The inlet conditions to the absorber are shown in Table I, and the outlet results in Table II along with the respective calculated values from TSWEET. As can be seen from this table, the operating conditions for the absorber were constant to within about 5% except for the lean amine temperature which varied from 120^{o}F to 97^{o}F. This temperature variation was due to the reduced flow rates through the lean amine cooler.

Table II
North Caroline Plant MDEA Modifications
Comparison of Experimental Results with TSWEET

Test	SWEETENED SALES GAS				Liquid Residence Time sec.	Rich Amine Loading mol/mol	
	H_2S Concentration PPM		CO_2 Concentration PPM				
	EXP	TSWEET	EXP	TSWEET		EXP	TSWEET
1	~0.6	0.70	1.85	2.11	3.51	.58	.51
2	~0.6	0.71	1.58	1.83	2.93	.55	.49
3	<0.1	0.44	1.34	1.37	2.45	.52	.52
4	<0.1	1.04	1.16	1.10	2.10	.46	.47
5	<0.1	0.39	1.13	1.17	1.99	.45	.49

Table II also shows the rich amine loading (mole of acid gas/mole of amine) as a function of the circulation of amine.

The absorber easily produced H_2S concentrations below 1/4 gr/100 SCF at all of the tested amine flow rates. The values calculated by TSWEET are also well below the 1/4 gr spec. As shown in Table II and Fig. 3, the CO_2 concentration in the sales gas varied from about 1.1% at 123 gpm to about 1.8% at 69.6 gpm. The CO_2 concentration calculated by TSWEET matched the data values almost perfectly at the 123, 116 and 99.8 gpm flow rates. At the 83.5 and 69.6 gpm flow rates the measured CO_2 in the sales gas was about 10% below the values calculated by TSWEET.

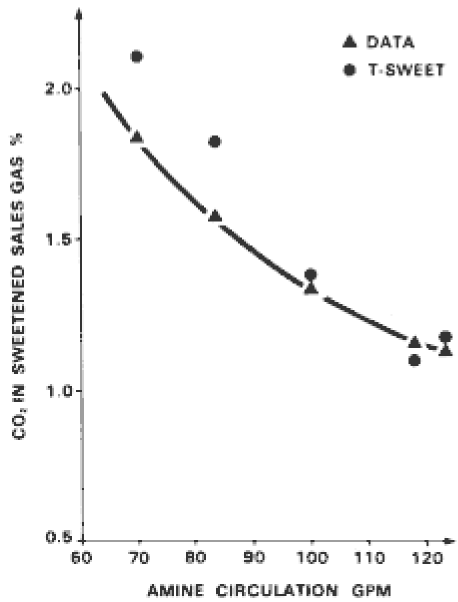

Fig. 3. CO_2 Rejection as a Function of the Amine Circulation

In addition to the data shown in Table II, temperature measurements were also made at several points through the absorber for each amine flow rate. The experimental temperature profiles are compared to the profiles calculated by TSWEET in Figs. 4-8. As can be seen from these figures, the shape of the temperature profiles calculated by TSWEET matched the shape of the actual profiles almost exactly. In addition, the maximum calculated temperatures occurred at the same location in the tower as the actual maximum for all cases. Although the calculated maximum temperatures of the rich amine were as much as 10 to 15^{o}F lower than the observed maximums for one or two cases, the absorber inlet and outlet temperatures agreed closely for all cases.

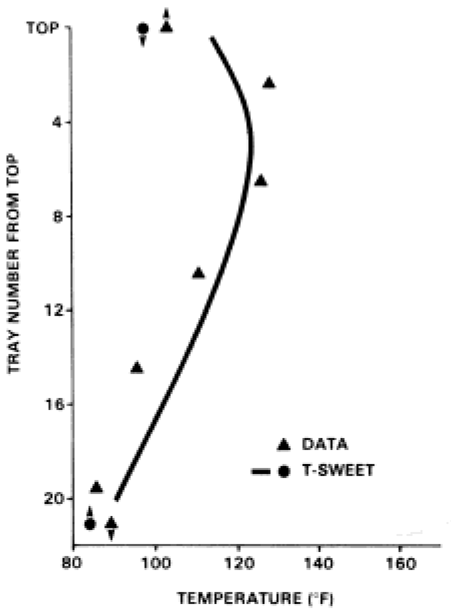

Fig. 4. Absorber Temperature Profile for Test Number 1, 69.6 GPM

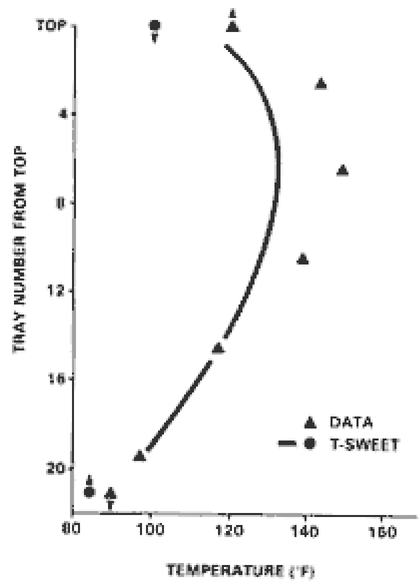

Fig. 5. Absorber Temperature Profile for Test Number 2, 83 GPM

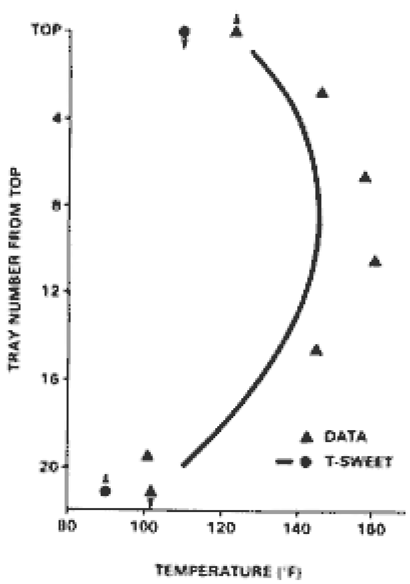

Fig. 6. Absorber Temperature Profile for Test Number 3, 100 GPM

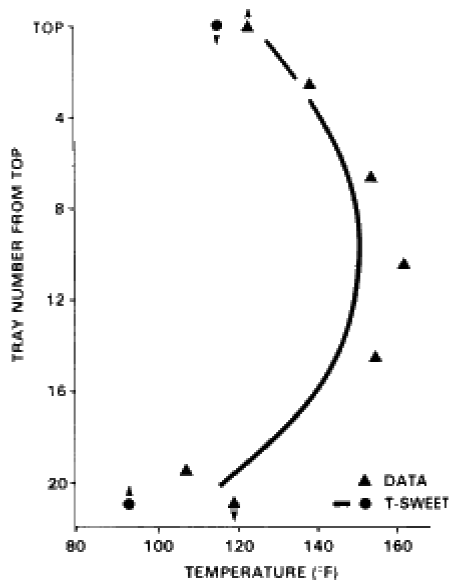

Fig. 7. Absorber Temperature Profile for Test Number 4, 116 GPM

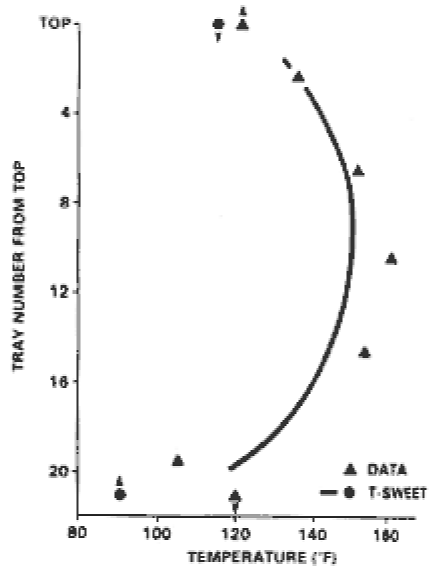

Fig. 8. Absorber Temperature Profile for Test Number 5, 123 GPM

SUMMARY AND CONCLUSIONS

Dome's North Caroline sweetening plant was the first plant in Canada to be converted from DEA to MDEA. The amine plant performed very smoothly and was debottlenecked to, at least, its original design capacity. A process simulation program called TSWEET was used as the basis for the conversion from DEA to MDEA. Performance data was taken for the absorber at several amine flow rates. A comparison of the performance data to the values calculated by the program showed that TSWEET was quite accurate and moderately on the safe side.

Dome intends to process gas from other sour reservoirs around the North Caroline plant, which will push the H_2S concentration in the feed gas from 50 PPM to about 2400 PPM. Computer simulations using TSWEET have shown that the amine plant will accommodate the 2400 PPM H_2S and easily produce 1/4 gr/100 SCF sales gas. Dome is also using TSWEET to investigate switching other sweetening plants to MDEA to improve the H_2S/CO_2 ratio and thereby improve the sulphur plant performance and efficiency.

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