Field Test Results Of The Physical Solvent N-Formyl Morpholine For Gas Treating Applications

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Introduction

NFM (N-Formyl morpholine) is proposed as a physical solvent for treating natural gas containing high concentrations of CO_2 and/or H_2S. Natural gas has wide range of acid gas concentrations, from parts per million to 50 volume percent and higher, depending on the nature of rock formation from which it comes. A contaminant removal process takes a mixed stream (combination of desirable and undesirable components) separates it into two or more streams (one of desirable components and others of undesirable components). The effectiveness of such a process for the removal of impurities from gaseous streams of light hydrocarbons (such as methane, CH_4, ethane, C_2H_6, propane, C_3H_8, butanes, C_4H_{10}, etc.) is a function of the composition of the gas to be processed, the specifications required of the cleaned gas, and the characteristics of the solvents used. In most situations the composition of both the gas to be processed and cleaned gas are set by nature and pipeline specifications. The characteristics of many solvents (poor selectivity, requiring low operating temperatures, high pressure requirements, high circulation rates, affinity for light hydrocarbons, high temperature regeneration procedures, etc.) used in contaminant removal processes can cause high operating costs and/or loss of valuable products. The NFM solvent systems discussed here designed to be more operationally effective than currently available systems for bulk and/or selective removal of impurities from light hydrocarbon steams.

Approximately 30% of proven reserves fall into this subquality natural gas category according to studies conducted by GRI[1,2]. Because of corrosiveness of acid gases in the presence of water and toxicity of H_2S and lack of heating value of CO_2, sales gas is required to be treated to meet the pipeline specification. It is necessary to remove carbon dioxide, CO_2, from the treated gas stream for a variety of reasons. If the gas is to be sold to the public, CO_2 must be removed from the gas stream to maintain the heating value of the gas. The heating value of most natural gas streams is about 1000 Btu per 1000 SCF. To stay above the minimum heating value, the gas sold to the public usually contains no more than 2% CO_2. In addition, if CO_2 and liquid water are introduced into the gas transmission lines, the corrosion rate in the gas lines can increase.

N-Formyl morpholine (NFM) is currently being tested for treatment of subquality natural gas because of its potential advantages of reduced refrigeration, higher capacity for H_2S and CO_2, less loss of valuable hydrocarbons, and lower operating costs compared with

other commercial physical solvents[3]. An experimental program to obtain data for evaluating NFM's gas conditioning and dehydration potential has included the following:

- Thermodynamic Properties: vapor-liquid equilibrium, auto-refrigeration, and density
- Transport Properties: viscosity, surface tension, diffusion coefficients, and volumetric mass transfer coefficients.
- Chemical Properties: thermal stability and corrosion
- Field experiments

Research Objective and Program Approach

The Institute of Gas Technology (IGT) is developing gas processing technology that will reduce gas processing costs for current production and allow subquality gas to be economically produced that would have been otherwise, not produced. The experimental program being discussed in this paper has been in progress since 1990. It has primarily focused on the evaluation of N-Formyl Morpholine (NFM), shown in Figure 1, as a physical solvent for the cost-effective upgrading of subquality natural gas to pipeline quality. The selection of NFM for this program was based on previous work conducted by IGT in the selective removal of hydrogen sulfide, and carbon dioxide from coal gasifier effluents. That work showed that the use of NFM resulted in a significant cost advantage over 107 other solvents for that application.

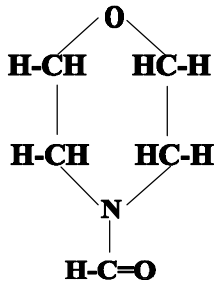


Figure 1. N-Formyl Morpholine ($C_5H_9O_2N$)

The project approach for the development of NFM process has been divided into following main categories:

Step I: Obtain vapor-liquid equilibrium, physical properties and additional published literature data

Step II: Obtain mass-transfer coefficients using 2" absorber/stripper apparatus. Calculate equation of state parameters and binary interaction parameters using VLE data

Step III: Develop a gas processing model using Aspen Plus simulation program and evaluate economic advantages of the NFM process compared to commercial physical solvent

Step IV: Design a pilot plant skid mounted field test unit and conduct field test experiments

Major Accomplishments

Laboratory Studies

Vapor-Liquid Equilibrium (VLE)

Figure 2 shows the VLE apparatus developed at IGT, which is capable of handling all sulfur species and operating from 25 to 3,000 psia and at temperatures from 60° to 300°F. This apparatus consists of a 1 liter vessel in which vapor and liquid phases are continuously circulated. On line phase sampling is conducted at system pressure and temperature. Small sample volumes (1 micro-liter samples for liquid and 1 milli-liter for gases) are withdrawn to ensure minimal disturbance of the system composition.

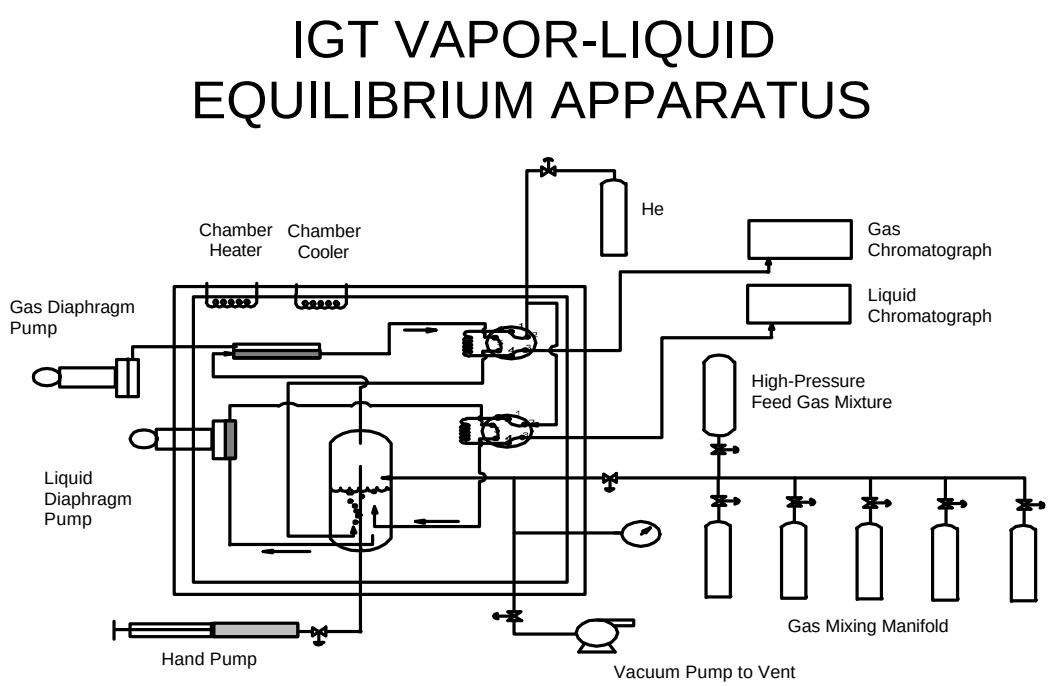


Figure 2. IGT Vapor Liquid Equilibrium Apparatus.

Over 1000 data points have been collected for mixtures of NFM and water over the following ranges of conditions:

Temperature, °F:	60-300
Pressure, Psia:	25-1,150

Gas Compositions:

Single Component	CO_2, H_2S, COS, C_3H_8, and C_4H_{10}
Mixtures	CH_4, CO_2, H_2S, C_2H_6, C_3H_8, C_4H_{10}, C_4H_{12}, and C_6H_{14}

The data collected indicates the following solubility ranking by K-values (mole fraction of component "A" in the gas phase divided by the mole fraction of that component in the liquid phase at equilibrium) at 6891 kPa (1000 psia), 289 to 322K (60° to 120° F), and for the compositions tested:

$$CH_4 < C_2H_6 < C_3H_8 < n\text{-}C_4H_{10} < i\text{-}CH_{10} < CO_2 < C_5H_{12} < H_2S < C_6H_{14}$$

This ranking indicates a potential for using NFM in selective processes. For example, in relative terms the solubility of H_2S is roughly three times greater than CO_2 at the conditions tested.

Computer Modeling

ASPEN™ Plus process simulation software package was used to regress VLE and other data to obtain the appropriate equation of state coefficients. Peng-Robinson, Redlich-Kwong-Soave, Redlich-Kwong-ASPEN™ and Redlich-Kwong-UNIFAC thermodynamic models were investigated. The model which was able to give the best fit to the data over the relevant range was Peng-Robinson which modified with binary interaction coefficients. These coefficients were fitted from the data collected using the maximum likelihood principle to formulate the objective function, and then minimizing that function by the algorithms of Deming and Britt and Lueke[4].

Computer Modeling of a Gas Processing Plant

In order to estimate the performance of NFM as a solvent system, a model of a gas processing plant was created using ASPEN™ Plus Process simulation package. Figure 3 shows the design of a selective gas processing plant in which H_2S is removed in the first loop and CO_2 is removed in a second loop. In this process H_2S concentrated in one stream which is sent for further processing while a relatively clean CO_2 stream is generated in the second loop.

SELECTIVE ACID-GAS REMOVAL PROCESS

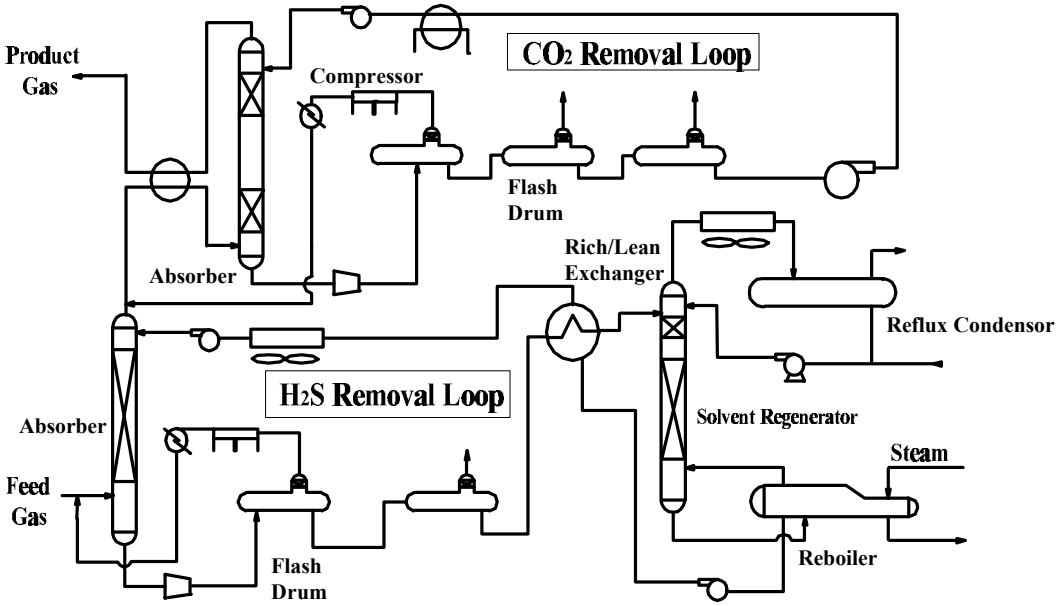


Figure 3. FLOW DIAGRAM OF SELECTIVE GAS PROCESSING PLANT

Table 1. GAS SPECIFICATIONS FOR COMPUTER MODELING

	Case A, Feed	Case B, Feed	Product Gas Specifications
Temperature, F	100	100	
Pressure, psia	1015	1015	
Flow, million SCFD	75	75	
Dry Basis Composition, mole %			
CH_4	91.0	59.0	
C_2H_6	0.0	4.0	
CO_2	6.3	35.0	< 2.0
H_2S	2.7	2.0	< 0.0004

Using the above design, simulations were performed for both a relatively low, and a high acid gas content feed composition. Table 1 shows the feed and product specifications while Table 2 summarizes the results of these cases.

Table 2. RESULTS OF SELECTIVE GAS PROCESSING SIMULATIONS

	Case A Product Gas	Case B Product Gas
Solvent	NFM	NFM
Solvent Circulation Rate, gal/hr	1936	2646
Temperature, F	52	55
Pressure, psia	1010	1010
Flow, million SCFD	69	46
Gas Composition, dry mole %		
CH_4	98.50	92.74
C_2H_6	0.0	5.7
CO_2	1.5	1.5
H_2S	0.00001	0.00001

Comparison between NFM and a commercial physical solvent system

As a reality check, a solvent manufacturer conducted simulations of the same Case A and B conditions using their proprietary models for a commercial physical solvent. Table 3 shows a comparison between NFM and the commercial solvent where the requirements of the commercial physical solvent is referenced as 100%. According to the models, there would be substantial savings in plant operating costs (40 to 50%), as well as in capital costs (15 to 30%). Since the commercial and NFM processes are very similar and there are substantial savings in operating costs, there may be a significant cost incentive to substitute for the commercial physical solvent with NFM in existing systems.

Table 3. COMPARISON BETWEEN A COMMERCIAL SOLVENT AND NFM.

Solvent	Commercial Solvent Case A and B	IGT's NFM Case A	IGT's NFM Case B
Circulation Rate	100%	94%	75%
Total Power Required	100%	70%	37%
Total Refrigeration Duty	100%	58%	55%
Total Heat Duty	100%	68%	57%
Total Construction Costs	100%	85%	70%
Total Operating Costs	100%	60%	47%

Taking our analysis one step further, a confidence interval analysis was performed. In this study the three main interaction coefficients that derived from our data was varied by plus and minus three standard deviations. This means that we can be 95% confident that the "true value" of the binary interaction coefficient lies in this range. Figure 4 shows the effects on the solvent circulation rate by varying the binary interaction coefficients one-at-a-time by plus and minus, three standard deviations around a base case. Case A was chosen as the base case for this study, since of the two conditions, this case showed the least advantage for NFM over the commercial physical solvent. As shown in this figure changing the interaction coefficients between H_2S-NFM and CH_4-NFM over the 95% confidence interval has little effect on total solvent circulation. However, varying the CO_2-NFM coefficient over the same confidence range does have a considerable impact on the solvent flow rates. In fact, over a large portion of the range, the NFM flow rate is estimated to exceed that of the commercial physical solvent, i.e., circulation rate greater than 100% of the commercial physical solvents.

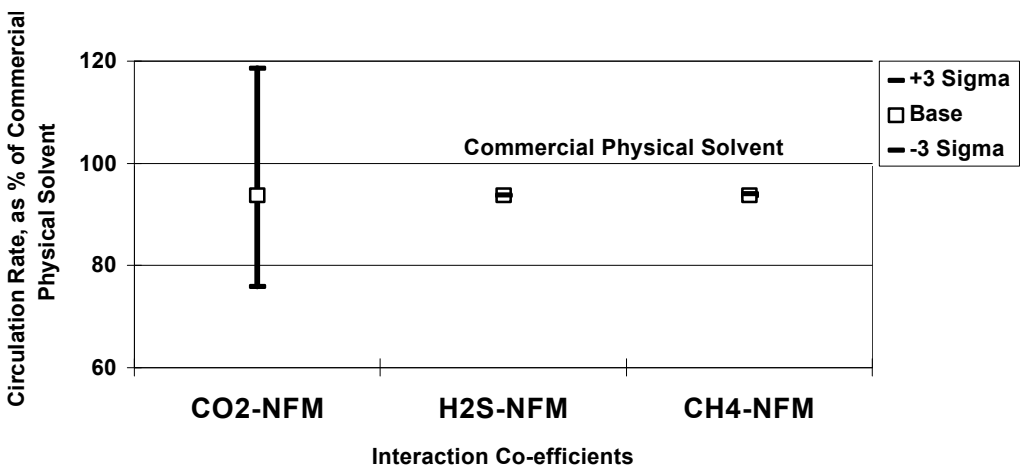


Figure 4. PARAMETRIC ANALYSIS OF INTERACTION COEFFICIENTS ON ESTIMATED SOLVENT CIRCULATION RATE.

Figure 5 shows the effect that these interaction coefficients have on operating costs for the same conditions (base, plus and minus three standard deviations).

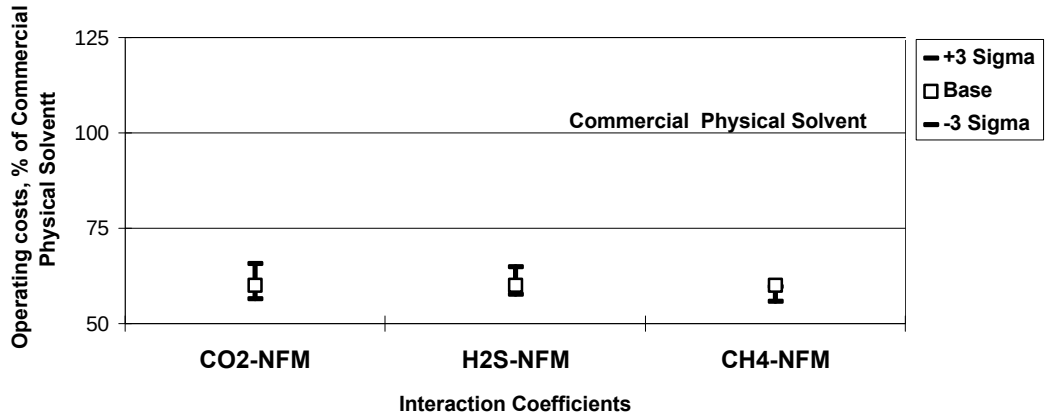


Figure 5. PARAMETRIC ANALYSIS OF INTERACTION COEFFICIENTS ON ESTIMATED SOLVENT OPERATING COSTS.

These results imply that although the circulation rate may significantly exceed that of the commercial solvent (by almost 20% in the case of the CO_2-NFM interaction coefficient variation), the operating costs were still significantly lower than those of the commercial physical solvent, i.e., in excess of 30%**.** As far as capital costs are concerned, the capital costs remained less than those for the commercial solvent by 10 to 15% over the 95% confidence interval. In summary, the statistical analysis of the data obtained imply a 95% confidence that the NFM solvent system will significantly out perform the commercial physical solvent in both new and retrofitted applications for gas sweetening processes. In addition to economic evaluations of NFM solvent by IGT, an independent study conducted by Krupp Uhde (IGT has entered into a technology development and commercialization agreement with Krupp Uhde GmbH, Germany) is also confirms IGT's findings as indicated in the following table 4.

TABLE 4. NFM OPERATING COST SAVINGS

	Acid Gas Content (mole%)	IGT Study	KK Study
Case A	CO_2 6.3%, H_2S 2.7%	40%	29%
Case B	CO_2 35.0%, H_2S 2.0%	53%	51%
Case C	CO_2 11.4%, H_2S 7.9%	-	31%

Field Testing

With the magnitude of potential savings estimated as indicated in Table 4, sponsors of this research program, Gas Research Institute, DOE, cofunding partners of IGT Sustaining

Membership Program, Krupp Koppers and industrial partners, Huntsman Chemical Company and Shell Western Exploration and Production Corporation (SWEPI) embarked on a field test program to confirm the earlier predictions which were based on laboratory bench scale apparatus. For the purpose of field testing at gas well-head site, a 10-gpm skid-mounted pilot plant was designed and constructed to test both physical and chemical solvents. The skid field unit as shown Figure 5, is equipped with a nominal 8-inch diameter absorption column. The unit will have a gas processing capacity ranging from 0.25 - 1.00 million SCFD depending on the acid gas content of the feed gas. The field testing was carried at SWEPI's Fandango plant site located in south Texas for a period of six months . The operating parameters of field tests using random and structured packing are indicated in the Table 5.

Figure 5. 10-gpm Skid-mounted pilot plant test unit

Table 5. OPERATING PARAMETERS FOR FIELD TESTS

PARAMETER	RANGE
Contactor Pressure, psig	500-1000
Contactor Temperature, °F	85-115
Flash Tank Pressure, psig	65-400
Feed Gas Flow Rate, MSCF/d	200-800
NFM Solvent Circulation rate, gpm	5-10
Reboiler Temperature, °F	330

Process Configuration and Test Program

The process flow scheme for IGT's pilot plant is very similar to that of the other conventional amine treating systems as shown in figure 6. The sour feed gas is contacted coutercurrently with lean NFM solution in a 8" OD absorber filled with random "dumped" packing (1" metallic pall rings supplied by Koch Engineering) with single top solvent entry point. Normally, the absorber pressure is maintained at 1000 psig, however for the purpose of obtaining data at various partial pressures of CO_2, absorber pressure is varied as indicated in table 5. The rich solvent from the absorber bottom passes to a flash drum operating at 65 psig where dissolved gases are flashed. The rich NFM solvent from flash drum is then exchanged with hot NFM solvent leaving the regenerator in order to reduce the reboiler load on the stripper and to reduce the amount of cooling needed for the lean NFM solvent. The acid gas absorbed by NFM in the absorber is removed in the regenerator. The lean NFM solvent is then passes through high pressure pump to the absorber.

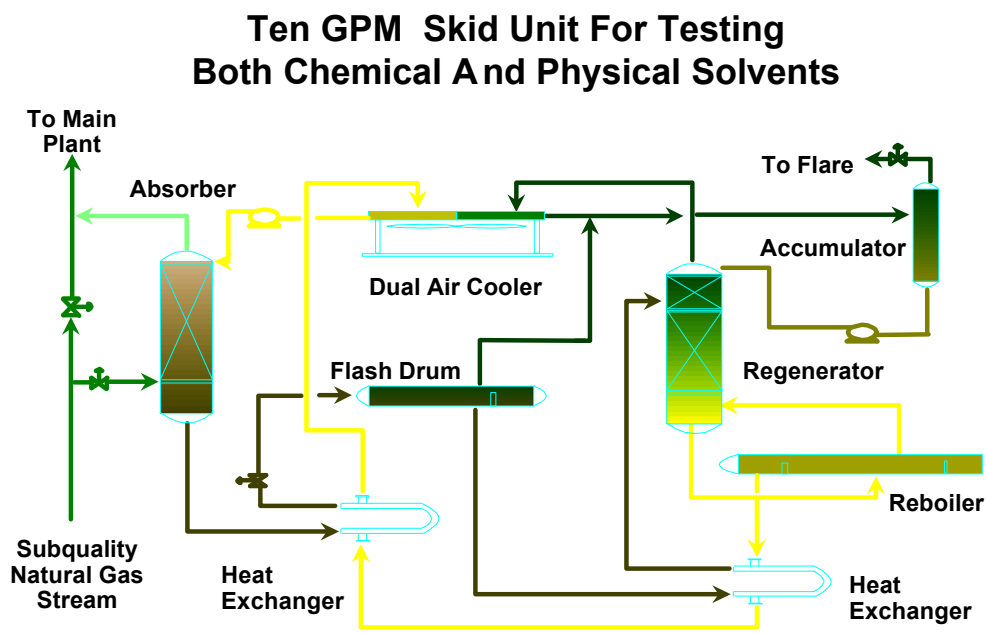


Figure 6. Process flow configuration for pilot plant

Pilot plant field tests were conducted using a slip stream from Shell's Fandango plant containing 15% acid gas. Normal operations were to be maintained during the test. Any variable change was not to cause changes in feed gas flow rate and NFM circulation rate. The boundary limits on the variables studied were limited to that conditions were required to maintain steady-state operation. For instance, the circulation rate is limited to 10 gpm due to limitation of pump capacity and distributor plate in the absorber. The lean solvent

temperature controlled by air fin cooler before pumping back to the absorber. Hence, the temperature approach at the best is 20 °F to the ambient temperature. This limited the range at which we could the study the contactor temperature. To avoid this, some of the experiments were conducted during the night to take advantage of cool temperatures. Basically, the variables studied were varied to the extent possible to the limits of the operating equipment and its accessories.

Five operational variables were studied: inlet sour gas flow rate, NFM solvent circulation tare, lean solvent temperature, reboiler temperature (NFM stripping rate) and flash tank pressure. The following five cases were studied using Shell's slipstream with 15% acid gas composition.

1. CO_2 absorption performance tests at fixed circulation rate with varying feed gas flow rates.
2. Reboiler tests to test regeneration quality of the NFM solvent with varying reflux ratio.
3. Tests to verify the effects of partial pressure of CO_2 on absorption.
4. Tests at varying circulation rates to verify hydraulic performance.
5. Reruns to check repeatability and reliability.

Pilot plant data was obtained from four gas streams: inlet sour gas, sweet residue gas, flash drum overhead gas, and acid gas from stripper reflux accumulator; and three liquid streams: high pressure rich NFM solvent with dissolved gases from contactor, rich NFM solvent from flash tank and lean NFM feed to the contactor.

Analysis of the gas streams was made on a gas chromotograph for complete component analysis. Two Varian GC's were exclusively used for on-line gas analysis. The tubing connections were made directly from pilot plant unit to the trailer unit containing analytical apparatus. The gas analysis was made on-line at pressure. One of the GC's is equipped with FPD (flame photometric detector) for analyzing low concentrations of H_2S with a capacity of measuring 1ppm concentration in gas streams and FID for measuring low concentrations of higher hydrocarbons. Though liquid analysis was done on-line, it was completed little differently from gas analysis. The liquid sample at a sample point at the field test unit is trapped in a sampling valve at pressure and then was connected to GC for analysis. The water content in the NFM solvent was also analyzed simultaneously using Karl-Fisher apparatus.

Test Results

A total of 37 separate data sets were taken using NFM solvent (95% NFM and 5% water by weight) and 1" pall rings (6 cu. Ft of random packing) in the contactor. At first, experiments were conducted at a fixed solvent rate i.e., 10 gpm and changing inlet sour gas flow at the rate of 100,000 MSCFD for each set of new conditions while maintaining contactor pressure at 1000 psig to study the absorption capacity of NFM solvent. The

purpose of these tests is not meet the pipeline specification of sweet gas, however to study hydraulic performance of the solvent in the contactor. The figure 7 shows that relationship between inlet sour gas flow rate to CO_2 gas specification in the sweet gas. As the figure 7 shows, there is a noticeable difference in product gas specification particularly at low inlet sour gas flow rates inspite of higher contactor temperature due to reboiler operation. This is due to cleaner lean solvent as a result of reboiler operation. However, at gas flow rates above 500 MSCFD, the difference is insignificant meaning that reboiler may not be necessary to achieve same acid gas loading as in case of reboiler operation. The field test data indicates, the absorbed CO_2 gas can be driven off with series of flashes including vacuum flashing avoiding full fledged reboiler.

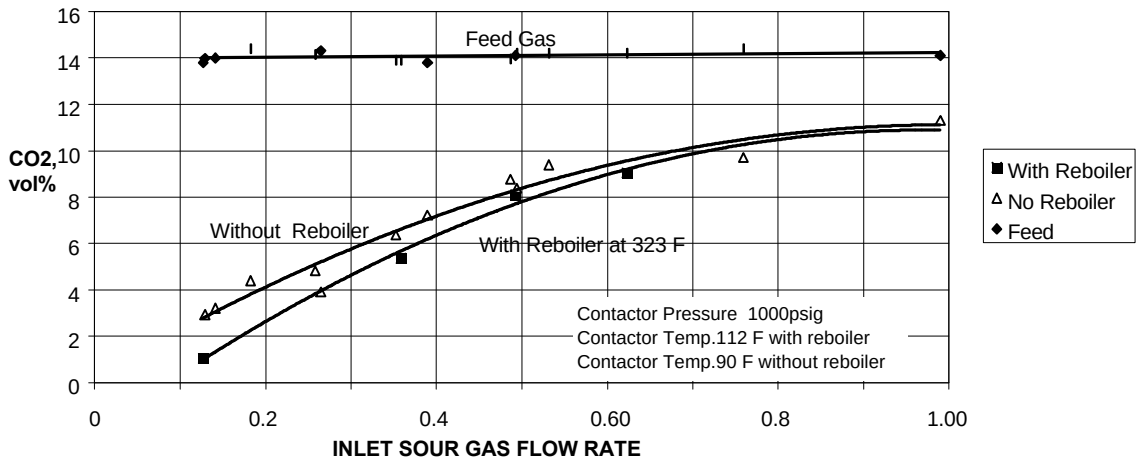


FIGURE .7

Figure 8 shows the relationship between the acid gas loading and gas to liquid ratio. The acid gas loadings obtained at pilot plant tests are comparable with present state of the art commercial physical solvents available to date despite the fact that the operating the contactor 60-80 °F higher than the commercial physical solvents during the pilot plant field tests. As the data shows, equivalent acid gas loadings can be achieved without any refrigeration system with NFM solvent.

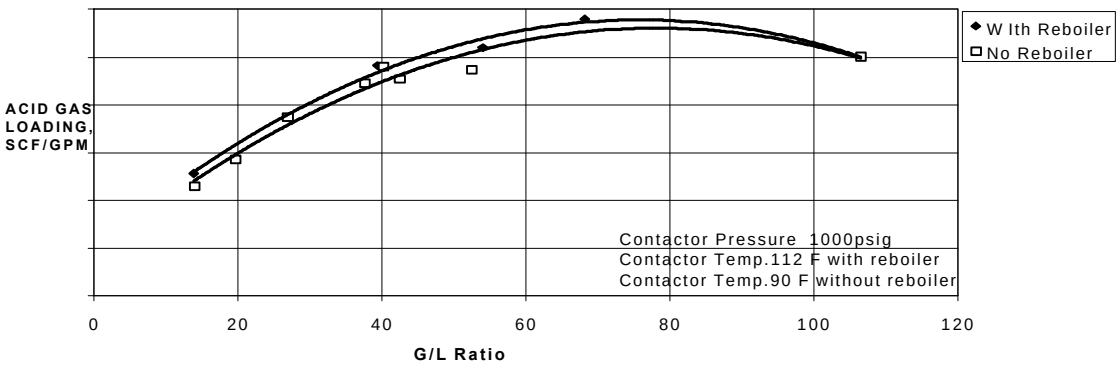
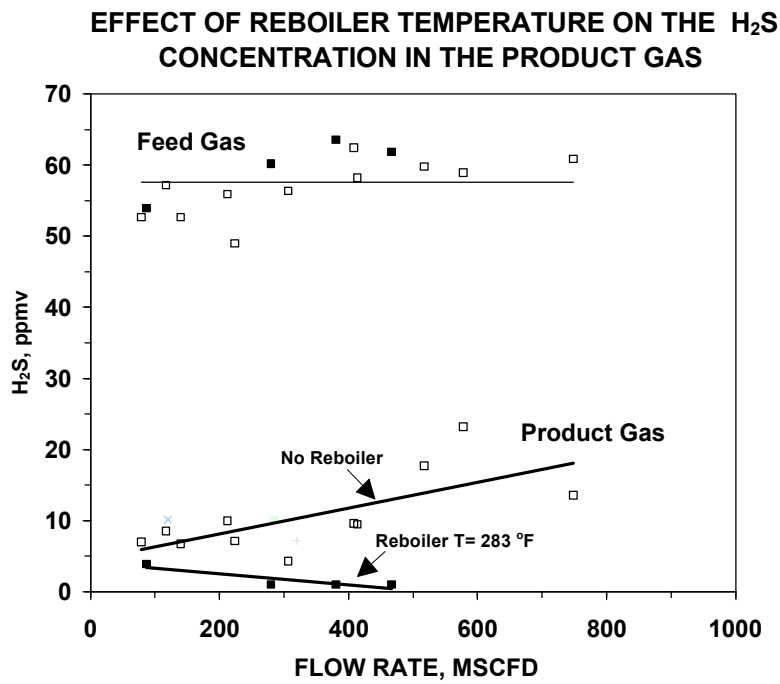


FIGURE. 8

Figure 9 shows the performance of reboiler on H_2S gas specification in the sweet gas. This data indicates that pipeline gas specification can easily met by reducing the H_2S level to less than 1 ppmv. Without reboiler operation, despite low packed-bed column height in pilot plant unit, significant reduction in H_2S was obtained i.e., reduced from 70 ppmv in the feed gas to 10-20 ppm.



Economic Benefit Analysis and Market potential

Based on the VLE lab studies, computer simulation of gas processing plant and field test studies at Shell's Fandango plant in south Texas, with the advantages such as no refrigeration, lower recycle compressor capacity and less absorption of valuable hydrocarbons, it is estimated that an operating cost savings of $29 million/year for the

existing plants as indicated in Table 6. These data were based on GRI Topical Report GRI-93/0342[6], "Business characteristics of the Natural Gas Industry," by Purvin & Gertz, Inc., May 1993. In the same report, it is also estimated that 175 new CO_2 removal plants needed by year 2000 in order to meet the demand. The savings could be significantly higher than indicated above if NFM can be used in new plants in addition to retrofits.

Table 6. POTENTIAL OPERATING COST SAVINGS WITH USE OF N-FORMYL MORPHOLINE FOR NATURAL GAS PURIFICATION

Process	Number of Plants	Avg. Plant Size	Total Gas Capacity, MMCF/d	Plants Changed Over, %	Operating Cost Savings, $/MCF	Total Annual Savings, $million/yr
Selexol	5	205	1020	80	0.04	10.7
Sulfinol	57	85	4678	30	0.03	13.8
Chemical	394	85	34295	2	0.02	4.5
Total	456					29.0

Conclusions

The natural gas industry expends substantial resources to remove impurities from subquality natural gas, so that it can be marketed or used directly. The NFM technology being developed here, according to experimental data, computer simulations of gas processing plants and pilot plant test data indicates substantial savings in capital costs and operating costs. Predictions of total operating cost savings for NFM process compared to current state-of-art physical solvent processes were indicated to be about 40% based on 15% CO_2 gas composition at 75 Mmscfd. The savings would be expected to be higher with higher acid gas concentrations. Comparison of computer simulations with published data for a gas processing plant indicate that 1.04 times more CH_4, 76 times more C_3H_8 and 32 times more C_4H_{10} remain in the marketable gas when NFM used in place of Selexol™,[5]. This characteristic of NFM increases quantity and heating value of sales gas and reduces the solvent regeneration costs.

Contract Information

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