

Pilot Tests Prove Ryan/Holmes Cryogenic Acid Gas/Hydrocarbon Separations

A. S. HOLMES AND J. M. RYAN

Koch Process Systems, Inc.

and

B. C. PRICE AND R. E. STYRING

ARCO Oil and Gas Company,

Division of Atlantic Richfield Company

ABSTRACT

Cryogenic CO₂/H₂S/hydrocarbon separation processes were tested in an ARCO Oil and Gas Co./Koch Process Systems pilot facility. Streams containing from 12% to 90% CO₂ were successfully separated to produce a marketable methane stream and a CO₂ stream with 2% or less methane.

Additionally, high NGL extraction (over 90% ethane recovery) was demonstrated. Pipeline quality methane (H₂S less than 1/4 gr/ccf or 4 ppm) and high pressure CO₂ with less than 100 ppm H₂S were produced from feeds containing up to 2% H₂S. Engineering studies show these processes to be commercially attractive for CO₂ enhanced oil recovery projects and naturally occurring high CO₂ gas sources.

INTRODUCTION

ARCO Oil and Gas Co. entered into an agreement with Koch Process Systems (KPS) in 1980 to conduct a pilot plant test program of a series of KPS-owned distillation technologies for the separation of sour natural gas mixtures. A pilot demonstration plant was built at Atlantic Richfield's gas processing facility at Covington, Okla. This joint development was completed in October, 1981. The processes tested have specific applications in:

1) Upgrading of the Btu content and quality of natural gas streams containing high concentration of acid gases (CO₂ and H₂S).

2) Treatment of hydrocarbon-rich sour gases where high NGL recovery is an important factor.

3) Processing of associated gases from enhanced oil recovery projects where the process used (CO₂ flood, fire-flood, inert gas injection) results in progressively increasing concentrations of the injection gas or byproducts in the separator gases.

These distillative separations are titled, "Ryan/Holmes Processes" after two KPS employee-inventors. These Ryan/Holmes separations all involve the use of an additive to provide a particular benefit to the distillation. The following three principal distillative separations were tested:

1) Separation of methane from CO₂. This separation uses an additive to avoid CO₂ freezing and/or otherwise enhance the distillation conditions.

2) Separation of CO₂ from ethane and heavier liquids. This separation uses an additive to break the CO₂-ethane azeotrope.

3) Separation of CO₂ and H₂S. This separation uses an additive to enhance the relative volatility of CO₂ with respect to H₂S.

Although a number of classes of materials are suitable as additives for the Ryan/Holmes separations, the use of natural gas liquids (NGL) was found to be advantageous for typical gas processing applications because of availability, compatibility, and to avoid introduction of foreign components. We will concentrate primarily on the use of various NGL mixtures in this presentation. A wide range of NGL compositions can be used as additives. This is beneficial from both design and operational points of view. However, it will be apparent, as we discuss the various separations, that certain NGL mixtures are favored for specific applications.

PROCESS PRINCIPLES

Separation of methane and CO₂

Based on their relative volatility, the separation of methane from CO₂ by distillation should be easy. The relative volatility of methane to CO₂ at typical demethanizer conditions is approximately 5 to 1; however, at demethanizer conditions, CO₂ co-exists primarily as vapor and solid phases in some section of the column if CO₂ is sufficiently concentrated.

Referring to Fig. 1, the problem of CO₂ solid formation in a distillation column becomes evident. This figure is a phase diagram for the methane-CO₂ binary.^{3,4,7,12} The single component lines for methane and CO₂ vapor-liquid equilibrium are shown as the left- and right-hand boundaries of the phase diagram ending at the critical points for these components. The unshaded area in between these two boundaries is the area of coexistence of equilibrium vapor and liquid phases of the binary mixtures. The shaded area in the lower left-hand portion of this figure represents the particular problem area where the phases in equilibrium consist of a binary vapor and solid CO₂. This means that any operation within this shaded area of the phase diagram will always have solid CO₂ present.

Because the tip of this solid CO₂ area extends to a higher pressure (approximately 705 psia) than the critical

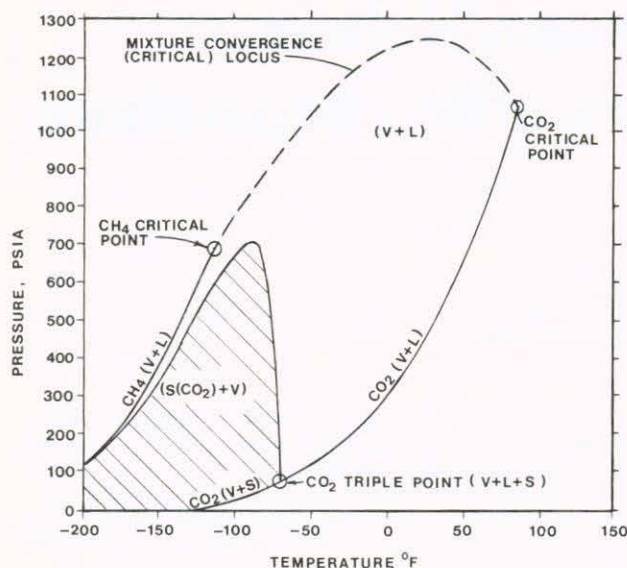


FIG. 1. Phase diagram—CH₄-CO₂ binary.

pressure of methane, it is not possible to go from a composition of high CO₂ to a composition of pure methane at constant pressure without passing through this solid CO₂ region. A number of combinations of single and double column systems^{5,9,10} operating at different pressures have been proposed in the literature to circumvent this problem. However, all of these schemes involve operation close to the methane critical, or the methane-CO₂ mixtures critical or close to CO₂ freezing conditions. These schemes also require high energy and capital. Therefore, they have been uneconomic compared to other CO₂ removal systems.

Figure 2 describes the same solid formation barrier in a different way by showing the solubility limits of solid CO₂ in CO₂-methane liquid mixtures. The solid line extending diagonally across the figure represents the solubility limit of CO₂. To the left and above this line, solid CO₂ will be formed. Conversely, below and to the right of this line, vapor-liquid equilibrium exists and no solid formation is observed. The curve lines shown are calculated tray-to-tray, point-to-point conditions for the liquid phase ranging from cold temperatures with low CO₂ content at the upper end of a column to warmer temperatures and high CO₂ content at the lower end of a column. The dashed portions are liquid compositions which ignore the possibility of solid formation. In fact, the conditions of the dashed portion exceed the solubility limit. The column will freeze in these regions and be inoperable.

As shown, unless one operates above the pressure of 705 psia (the approximate tip of the solid CO₂ boundary as shown in Fig. 1), the distillation will always pass through the solids formation zone in order to go from a mixture containing high CO₂ to pure methane. If, for example, one operates at 715 psia, it is possible to avoid solid CO₂ formation. However, in this case, the limit on methane product purity is set by how close to the mixture critical one wishes to operate. The mixture critical is 2% CO₂. The practical limit would probably be 5 to 15% CO₂.

The Ryan/Holmes approach to this distillation is to add a suitable agent to the condenser or the top portion of the distillation column in order to significantly alter the

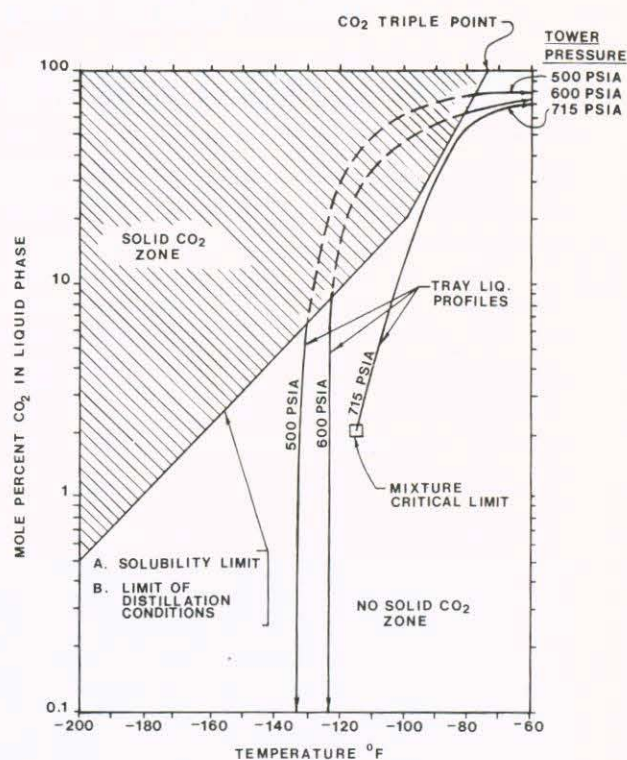


FIG. 2. Distillation profile—CH₄-CO₂ binary.

solubility characteristics of the system. For gas processing operations, these additives are normally simple mixtures of C₃+ hydrocarbons which are obtained by distillation and separation from the feed mixture itself.

Figure 3 gives an example of a Ryan/Holmes demethanizer column with a pure n-butane additive. This figure is similar to Fig. 2. The same solid diagonal line from Fig. 2 is seen as the most conservative boundary that one could draw from all of the available data on CO₂ solubility.^{1,6} The solid tray profile line shows a binary C₁-CO₂ distillation without additive producing a methane top product containing 2% CO₂ and a bottoms product containing less than 1% methane. As shown, operating conditions of this column pass through a significant portion of the solid CO₂ formation region. This indicates that a distillation would not be possible and that solid CO₂ would form inside the column.

The next curve to the right shows the significant improvement in column operation with only a small amount of n-butane added to the condenser. The amount of butane is 4 moles per 100 moles of feed, and the tray profile barely enters into the freeze zone. Subsequent distillation curves show further shifting away from freezing as additional amounts of n-butane are added to the column. Therefore, the designer or the operator can specify a closeness of approach to freezing and there is a corresponding amount of additive to be added to the top of the column.

Figure 4 goes a step further in illustrating the role of additive for avoiding freezing. In this figure, the actual freeze line is drawn to the left and above the most conservative freeze line that we had before. This actual freeze line

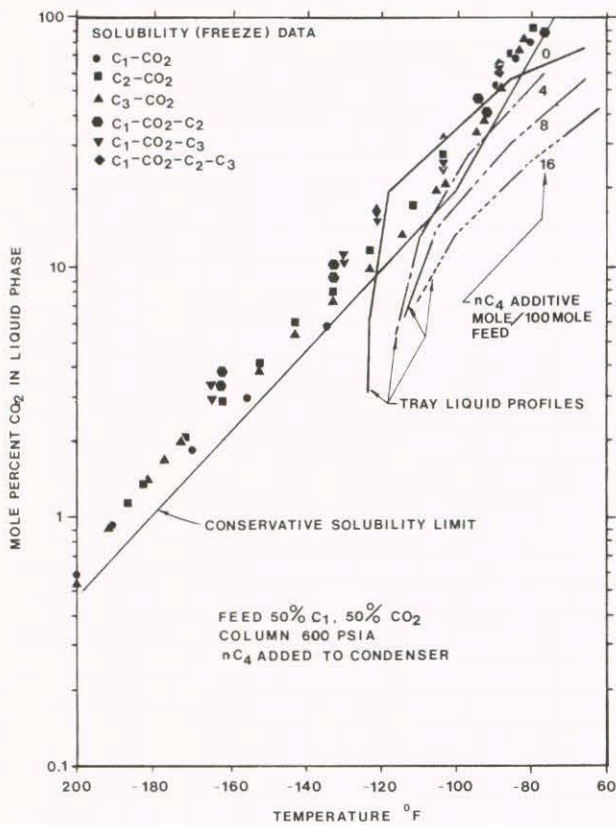


FIG. 3. Distillation profile—binary feed with nC_4 additive.

is based on data for certain applicable ternary systems of methane, CO_2 and n -butane.⁶ This illustrates the beneficial shift for multicomponent systems which include C_2 +hydrocarbons in addition to methane and CO_2 . This means that with small amounts of n -butane added to the system, one can operate a distillation and be much further from freezing than would be indicated by the C_1 - CO_2 data only.

Other NGL hydrocarbons demonstrate similar behavior. The tray profiles shown on Fig. 4 are based on a multicomponent feed. As shown, 8 moles of additive per 100 moles of feed are about the right amount to keep the 0.98% CO_2 overhead operation out of the conservative freeze zone. The 2.4% CO_2 overhead profile is just inside the conservative freeze zone, but nonfreezing relative to the freeze limit for butane-containing mixtures. The 2.4% profile shows that the closest approach to freezing occurs in the condenser (point "C") whereas, in contrast, the 0.98% profile shows the closest approach on theoretical tray 1.

In the demethanizer, the volatility of methane relative to H_2S is extremely high. In separating methane from CO_2 to normal pipeline quality (less than 2% CO_2), pipeline quality for H_2S is easily achieved. Therefore, the Ryan/Holmes demethanizer operation achieves both acid gas removal specifications simultaneously.

Other advantages of NGL-based additive for the demethanizer have also been observed:

1) Additive significantly raises the operating temperatures of the distillation column. This has the effect of lowering refrigeration horsepower requirements.

2) Additive increases the methane/ CO_2 relative volatility above that for the binary system.

3) Additive permits higher pressure operation. (The critical pressure of the mixture is significantly raised in the multicomponent system above that for the binary.)

Separation of CO_2 from ethane-plus hydrocarbons

The distillative separation of ethane from CO_2 is limited by the formation of an azeotrope between these components at an approximate composition of 67% CO_2 and 33% ethane.^{2,8} (An azeotrope is a constant boiling mixture whose vapor composition is identical to its liquid composition, thus precluding further separation by conventional distillation.)

The azeotrope phenomenon is represented in Fig. 5. The solid curves represent the phase behavior of the binary CO_2 -ethane system. The lower curves represent the normal binary system at 335 and 578 psia. The binary is a minimum boiling azeotrope with the approximate composition of two-thirds CO_2 , one-third ethane. It is interesting that this azeotrope does not significantly change in composition with different operating pressures. Therefore, distillations from either side of the azeotrope will be limited by the azeotrope composition.

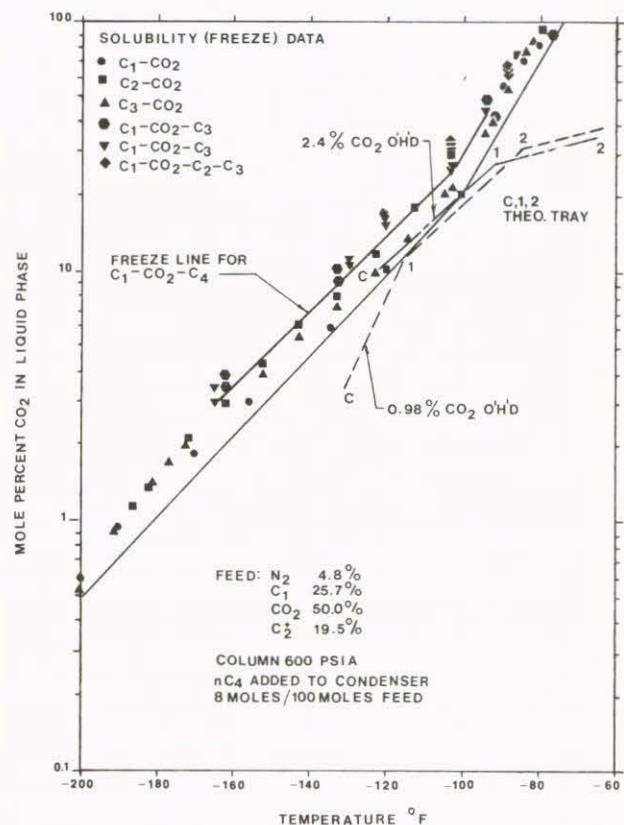


FIG. 4. Distillation profile—multicomponent feed with nC_4 additive.

A process is needed to resolve the ethane-CO₂ azeotrope because the bottoms product from a Ryan/Holmes demethanizer contains the CO₂ and all the ethane and heavier hydrocarbons that are in the feed. In cases where the feed contains substantial quantities of ethane, it is desirable to recover ethane with the other NGL components as a salable product. A typical bottoms composition from the demethanizer column is shown as the dotted line in Fig. 5. This figure would indicate, therefore, that one could make a pure CO₂ product as a bottoms product from the distillation column but would be limited in the overhead product to the azeotrope composition which would contain essentially all of the ethane which was in the feed.

A number of agents are suitable as additives to a distillation column to eliminate the formation of the ethane-CO₂ azeotrope. One class of Ryan/Holmes agents which is particularly suitable for gas processing operations is a mixture of light hydrocarbons such as butanes and heavier hydrocarbons. The upper dashed phase envelope in Fig. 5 indicates the behavior of a multicomponent feed distilled with a multicomponent C₄+ additive plotted on a CO₂-ethane pseudo-binary basis. All ranges of composition from 0 to 100% CO₂ can be achieved in this mode of distillation.

To effect this separation, the additive is normally introduced several trays from the top of the column. Therefore, the column has three zones:

- the bottom zone below the feed
- the top zone above the additive introduction point
- the middle zone below the additive introduction point and above the feed

The primary CO₂/C₂ distillation is actually carried out in the column below the additive introduction point. It is in this area that the relative volatility (α) of CO₂ to ethane is actually reversed, remaining above 1.0, and the azeotrope is circumvented. Rather high CO₂/C₂ relative volatilities are obtained at all points of the column below the additive introduction point.

The top portion of the column above the additive introduction tray represents a knockback zone to reduce the concentration of additive in the CO₂ product. It is interesting to note that immediately above the additive introduction point the relative volatility reverses (i.e., α CO₂/C₂ < 1).

The same additive compositions that are effective for demethanizer operation can be used for the CO₂-ethane separation. These same mixtures can also resolve other acid gas/light hydrocarbon azeotropes which might be encountered in gas processing or in other applications. Other additive advantages, such as higher than conventional operating temperatures and critical pressure alteration, are also achieved by operation in this manner.

Separation of CO₂ and H₂S

Many gas processing applications involve feed gas contaminated with both carbon dioxide and H₂S. When H₂S is present in the feed, it must be thoroughly removed from all product streams. Typical methane sales gas specifications require less than 1/4 grain of H₂S per 100 cu ft of product gas. Typical carbon dioxide product specifications require less than 100 ppm H₂S in the CO₂ product. Finally, H₂S is normally converted to elemental sulfur by the Claus process. Typical Claus plant feeds are practically limited to a molar ratio of CO₂ to H₂S of no more than 3 to 1. The required separations can be accomplished by the Ryan/Holmes processes.

In the separation of CO₂ from H₂S to meet safety requirements for the CO₂ product, the distillation is much more difficult. This is because the relative volatility between the two substances is quite small without additives. While an azeotrope between CO₂ and H₂S does not exist, vapor-liquid equilibrium behavior for the binary approaches azeotrope character at high CO₂ concentrations.¹¹ Improved separation is obtained by the addition of n-butane (or other suitable additives) to the system.

In the presence of additive, the Ryan/Holmes column separating CO₂ and ethane also benefits from a significant enhancement in the separation of H₂S from CO₂. This allows us to produce the carbon dioxide product at substantially less cost than would be otherwise possible without the additive present. In fact, it permits us to independently operate the carbon dioxide column to meet three separate criteria simultaneously:

- The purity of CO₂ with respect to ethane and H₂S.
- The recovery of ethane and higher hydrocarbons as a product.

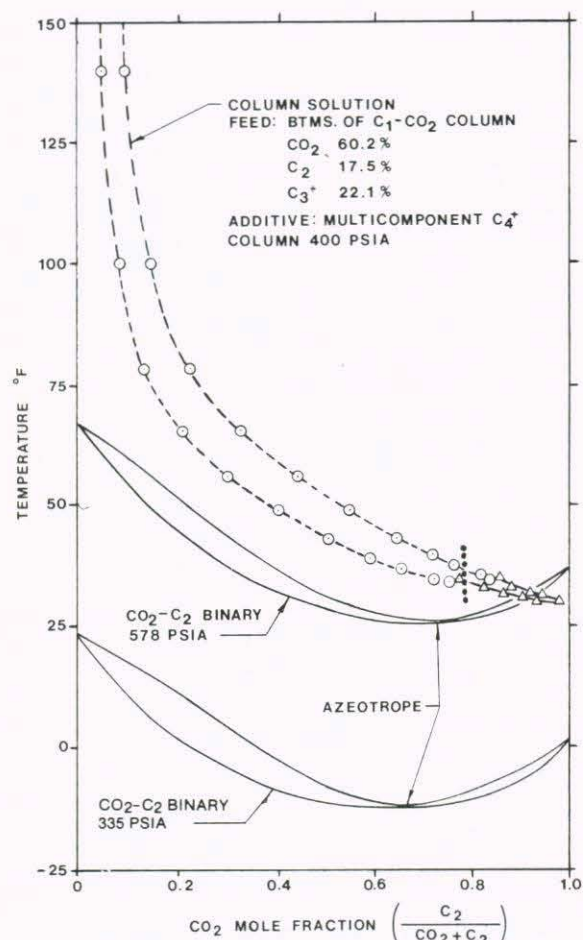


FIG. 5. Vapor-liquid equilibria—CO₂-C₂.

—The ratio of CO_2 to H_2S in the bottoms product. (This ultimately is the ratio of CO_2 to H_2S that will be removed and fed to the Claus plant.)

Typical Ryan/Holmes flow schemes

It is now possible to discuss several typical Ryan/Holmes flow schemes based on the previously discussed separations using NGL based additives. Figure 6 describes a flow scheme which could be used for an enhanced oil recovery project (i.e., varying CO_2 content in the feed and high NGL content which is to be recovered to the maximum economic level). As shown, this system consists of three columns. Column 1 is the Ryan/Holmes demethanizer. Column 2 is the Ryan/Holmes CO_2 product column, and Column 3 is the NGL product column (additive recovery column).

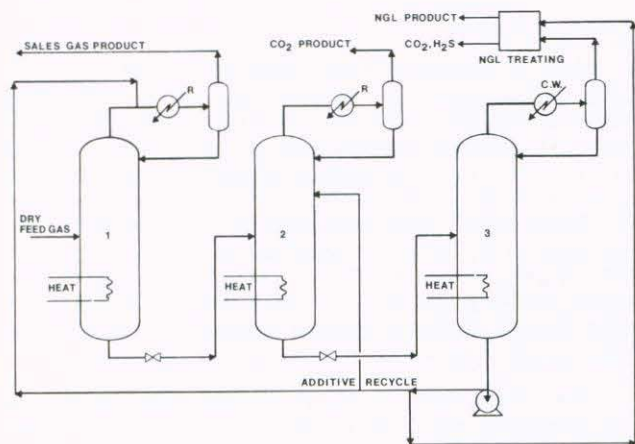


FIG. 6. Ryan/Holmes process—EOR plant.

Dry feed gas enters the Ryan/Holmes process area and is cooled by both appropriate cold products and by refrigeration before entering the demethanizer column. The NGL mixture which has been optimized for this particular application is added in the condenser of the demethanizer column. Overhead product sales gas is produced at essentially column operating pressure (normally 450–650 psi) and sent to the battery limits after heat exchange. (It should be noted that for LNG projects, this overhead product could be fed directly to the LNG plant resulting in significant energy and capital savings because of its low temperature and high pressure condition.)

The bottoms from Column 1 is fed to the CO_2 recovery column (Column 2) after suitable heat exchange. The additive NGL mixture is introduced to the column several trays down from the top. In this column the CO_2 product meets the required hydrocarbon and H_2S content specifications. This CO_2 product is produced at essentially the column operating pressure (normally in the range of 350 to 550 psig).

The bottoms product from Column 2 is fed to the NGL recovery column (Column 3). CO_2 has been stripped from this stream in Column 2 to the required ratio of CO_2 to H_2S . Column 3 functions to produce a light hydrocarbon overhead product stream which contains all of the H_2S and CO_2 fed to the column. It also produces a bottom stream which is suitable for use as an additive. A slip

stream is taken from the bottom stream to remove the net C_4+ hydrocarbons that were contained in the feed. This slip stream is mixed with the net overhead product to become the NGL product from the process.

The NGL product can be treated either as a liquid or vapor by an amine system to remove the acid gas content. It should be noted that this sweetening step is significantly less expensive than the original feed treatment would have been. This is because the NGL stream is very small in quantity and the bulk of the CO_2 has already been removed from the stream. The separated acid gases would be fed directly to a Claus plant for conversion to elemental sulfur byproduct.

Figure 6 represents a typical arrangement for a naturally occurring lean gas from a low Btu-gas field. However, in this type of application, the primary separation is between methane and CO_2 in the first column and between CO_2 and H_2S in the second column. This second column then becomes significantly less costly than in the case of rich EOR feeds where CO_2 -ethane azeotrope breaking was required.

There are many other combinations of Ryan/Holmes distillations that can be envisioned. Each application must be evaluated as to the optimum configuration. The following figures illustrate some of the variations which we have devised.

Figure 7 shows a scheme for processing a naturally occurring lean gas when H_2S is not present. In this case, only two columns are required, the second column being an additive recovery column which operates as a conventional distillation. This is the least expensive configuration for the process.

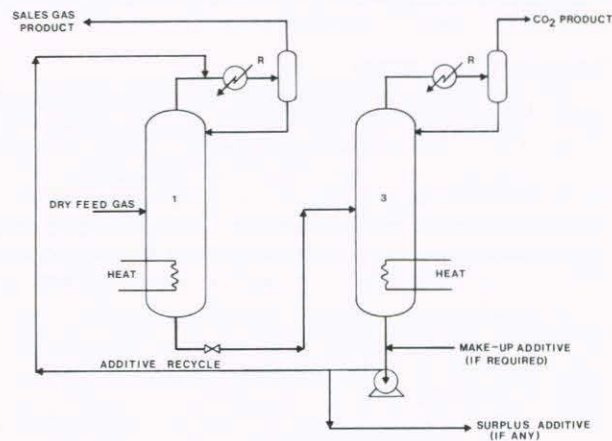


FIG. 7. Ryan/Holmes process—low Btu gas (no H_2S).

Figure 8 demonstrates a process arrangement wherein separation between methane and CO_2 is not required. This is applicable for situations where the combined methane- CO_2 overhead can either be reinjected or burned directly as a low Btu fuel. Alternatively, this methane- CO_2 overhead can be further processed by conventional distillation to produce a 7–800 Btu methane fraction or by Ryan/Holmes distillation to produce a higher purity methane product. Ethane and heavier hydrocarbons are recovered in the bottoms of this column and processed in the additive recovery column as for other cases.

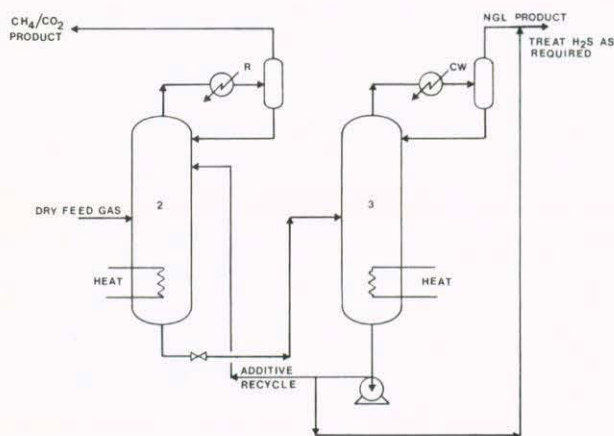


FIG. 8. Ryan/Holmes process—combined CH₄/CO₂ product.

DEVELOPMENT

In early 1980, Atlantic Richfield and KPS agreed to study phase equilibria and to conduct pilot plant tests relative to prospective full-scale field applications for the KPS/Ryan/Holmes processes. A major objective of the laboratory work was to obtain experimental data for certain regions where none was available. The primary objectives of the pilot plant were to prove that the C₁-CO₂ separation was possible without freezing problems and that the azeotrope of CO₂ and C₂ could be broken.

Laboratory program

The laboratory program consisted of multicomponent phase equilibrium cell experiments. For the separation of C₁ and CO₂ at low temperatures (below -70°F), avoidance of freezing is a major consideration. Measurements were made of the freezing points of mixtures derived from process simulation of multicomponent distillations in which NGL-based additive was used to prevent freezing. A visual cell was used so the freezing could be observed directly.

At pressures less than the critical pressure of methane, all mixtures tested froze if no additive was present. A small amount of additive would prevent freezing for the highest pressure (and correspondingly, warmer) operations. Additive requirements increase as temperature and pressure decrease. The nature of the freezing process was dramatically affected by the presence of additive. Without additive, a great deal of solid phase formed in response to a small drop in cell temperature. With additive present, less solid phase formed and the mixture took the form of a slurry.

According to the phase rule, a binary system exists as three phase only at phase transition boundaries. Away from the transition boundary there can only be two phases, namely vapor and liquid on one side of the transition changing to vapor and solid on the other side of the transition boundary. With additive present, there are more than two components. Vapor, liquid and solid phase can

coexist which accounts for the slurries observed in the tests.

We also measured K-values ($K \equiv y/x$) and relative volatility values, α ,

$$\alpha = \frac{K_{C_1}}{K_{CO_2}}$$

at conditions 10°F warmer than the freezing point for mixtures including multicomponent additive. α -values obtained experimentally were somewhat more favorable than α -values predicted from equations of state generally used in the gas processing industry (Soave-Redlich-Kwong and Peng-Robinson). Probably the reason for the deviation is that the traditional equations of state have their parameters adjusted to fit data where the CO₂ concentrations are relatively low as is typical of conventional cryogenic operations.

Most of our equilibrium data were obtained on the CO₂/C₂-H₂S separation because no data are available for the compositions predicted to occur in the distillation column. These compositions cover a range of CO₂/C₂-H₂S compositions but with significant amounts of C₄+ liquids present. We found the azeotrope is broken or reversed, that is, CO₂ is always more volatile than C₂. Technically, 100% recovery of C₂ in the column bottom product can be obtained while producing CO₂ completely devoid of C₂ overhead. At the same time, the relative volatility of CO₂ to H₂S is considerably enhanced making possible complete elimination of H₂S from the CO₂ produced overhead.

Concerning the CO₂/C₂-H₂S separation, we checked the generally available equations of state for mixtures (Soave-Redlich-Kwong and Peng-Robinson). In almost every case, these predicted more C₂ recovery and more thorough H₂S elimination than the laboratory results. We have used the laboratory data to establish a good fitting set of parameters for the equations. These specially fitted equations give good agreement with our pilot plant data and will be used for scaled-up designs for full-sized field CO₂ processing units.

Pilot plant

In early 1981, a pilot plant for the Ryan/Holmes processes was installed at ARCO's Covington, Okla., gas processing facilities. Figure 9 is a process schematic of the

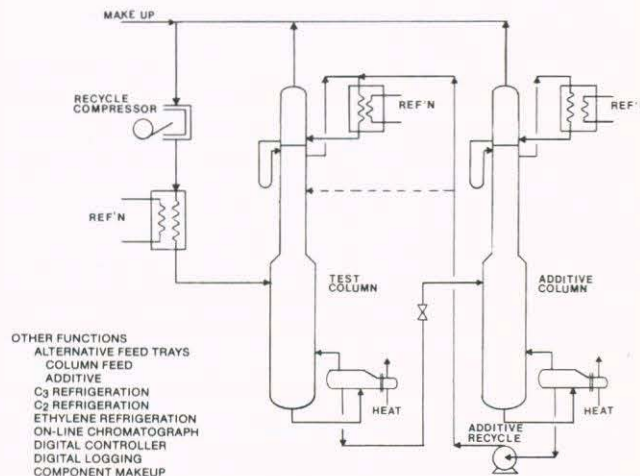


FIG. 9. Ryan/Holmes process—pilot plant.

pilot plant. There are two columns. The first column is our test column for performing either the C_1/CO_2-H_2S or the CO_2/C_2-H_2S separation. The bottoms of the first column flow to a second column whose purpose is to recover C_4+ as a bottoms product for recycle as an additive for the test column. The overhead vapor product of each column returns to the recycle feed compressor and then into the test column. Feed composition is adjusted by adding various components and venting off various points as appropriate. In most cases, the pilot plant was charged and compositions maintained by adding:

- 1) rich dehydrated gas (before NGL extraction)
- 2) lean dehydrated gas (plant residue gas)
- 3) raw NGL mix (dehydrated)
- 4) CO_2 .

Both columns have overhead condensers and reboilers. The test column is instrumented with temperature points and vapor sample taps on every other tray as well as on the overhead and bottoms streams. Additive could be fed to any of several points in the upper part of the test column, including the partial condenser.

Figures 10 and 11 are photographs of the pilot plant. In Fig. 10 the distillation columns can be seen inside the 10 ft $\times$ 10 ft $\times$ 60 ft framework. The framework also contains the heat exchangers, refrigerant vessels and additive recycle pump. The online process chromatograph is housed in the small aluminum building in the foreground. To the right and rear are the package propane and ethylene refrigeration skids and the recycle gas compressor. Figure 11 shows a view in the control room. From left to right are the digital



FIG. 10. Pilot plant at ARCO, Covington gas plant.



FIG. 11. Pilot plant digital controllers.

data logger (partially visible), the computer controller operator CRT station, the computer controller frame housing the microcomputer, and the output facilities of the online process chromatograph.

Table I lists the pilot plant general capabilities and chronology. The pilot plant results consisted of material balances and operating data. The unit is highly automated and instrumented. Operating conditions were usually quite stable. First, the compositions were adjusted and stabilized. Next, 2-6 hr were usually required to establish steady conditions. The material balance runs took 6 to 24 hr. An online process chromatograph gave a cycle of five stream analyses (N_2 through C_6+) in 1.5 hr. The digital controller unit not only accomplished closed loop and cascade controls but provided flexible and complete data logging, integration and trending.

Table II shows the resulting separations. Relative to separation of C_1 from CO_2 and H_2S , the test column overhead methane fraction (residual gas) was readily produced to sales gas objectives with 0.5 to 3.0% CO_2 and contained much less H_2S than 1/4 grain per 100 cu ft (4 ppm). Alternatively, feed quality for LNG production was achieved having 10 to 100 ppm CO_2 and satisfactory H_2S content. Such results were obtained using ethylene refrigeration in the overhead condenser (temperatures -110 to $-130^\circ F$) and also using only propane refrigeration (-30 to $-40^\circ F$). Even with 2% H_2S in the feed, sufficient fractionation to

TABLE I.
Pilot Plant Chronology

2-80	Agreement to start design Site Selection: ARCO Oil and Gas Co. Covington Gas Plant 600,000 SCFD nominal feed rate 750 psig column design pressure Can generate and test virtually any feed Koch: Total engineering, procurement, fabrication ARCO Oil and Gas: Site erection, operation
12-80	Koch ships skids
2-81	Mechanical installation complete
4-81	First tests
10-81	Complete Pilot Plant test program
11-81	Koch buy-back of Pilot Plant
2-82	Relocation to Koch Corpus Christi Refinery
6-82	(Planned) Resume test program at Koch Refinery

TABLE II.
Pilot Plant Program Results

MODE I OPERATION	MODE II OPERATION
Methane overhead	CO₂ overhead
CO ₂ 10 ppm to 3%	C ₂ recovery 50 to 98%
H ₂ S << 3 ppm (¼ gr/CCF)	H ₂ S 5 to 100 ppm
Bottoms	Bottoms
C ₁ /CO ₂ 0.002 to 0.05	CO ₂ 0.05 to 3%

meet the CO₂ specification resulted in more than adequate removal of H₂S. Ethane separation from the methane stream was high, typically above 99%. Even in the presence of substantial quantities of N₂, additive functioned to avoid freezing. In one particular material balance run, CO₂ in the methane fraction was 0.5% at an overhead temperature of -120°F even though there was 50% N₂ present.

Relative to the bottom product of the test column, the separation objective is the amount of light key, C₁, present which will subsequently be produced as an impurity in the CO₂ product. Typically, we achieved 0.2 to 5% C₁ relative to the CO₂.

Relative to the separation of CO₂ from C₂ and H₂S, the recovery of C₂ in the bottoms product ranged from 50 to 98%. H₂S elimination from the CO₂ product roughly parallels C₂ recovery but at a higher degree of elimination. We realized H₂S concentrations of 5 to 100 ppm in the CO₂ product. Our objective was 100 ppm H₂S. This Ryan/Holmes separation can be designed and operated to meet a C₂ recovery specification or an H₂S elimination specification or both. The bottom product of this column contains practically all the H₂S present in the feed (if H₂S is present). The CO₂ content can be specified to give CO₂/H₂S ratios tailored to Claus plant criteria.

If H₂S is absent, the CO₂ content of the potential ethane-propane mix can be specified; typically 1% or less is

required. The range of CO₂ concentrations in the bottoms stream from the test column was 0.05 to 3%.

Table III summarizes the achievements of the pilot plant test program and lists some of KPS's future objectives. The pilot plant demonstrated that product purities and specifications can be attained easily. Stability was excellent under all conditions. Specialized control and operating strategies were developed in order to manage the additive flow as required by the Ryan/Holmes processes; these control concepts can be readily incorporated into an instrument control system for a commercial plant.

TABLE III.
Pilot Plant Conclusions

Accomplishments:

- Obtained good separations C₁/CO₂, C₁/H₂S, CO₂/C₂, CO₂/H₂S
- Proved operating stability
- Capable of recovery from freezing
- Pilot Plant results confirm
 - Thermodynamic model
 - Additive and energy requirements
 - Can scale up designs

Future Objectives:

- Hydraulic tray and packing tests
- Other separations
- Available to service full scale plants
- Available for special customer testing

Freezing was shown always to be a basic underlying problem relative to ethylene refrigerated C₁/CO₂-H₂S separation. In all cases, stepwise reduction of additive flow rate always resulted in instability and freezing. In no case were we able to operate without additive. On the other hand, sufficient additive flow rate succeeded completely in avoiding instability. When freezing and the onset of instability were encountered, increases in additive flow rate were sufficient to restore stable operation. In a few cases, complete plugging of the overhead partial condenser was deliberately caused. Back pressuring the refrigerant ethylene vapor return line to approximately 100 psig loosened the solid mass and increased additive flow resolved that problem obviating a need for lengthy warmup through the exterior insulation.

We analyzed the material balance runs by process simulations based on our special (fitted to laboratory V-L-E data) equation of state. Good agreement was obtained for product compositions, recoveries, additive requirements and energy requirements, which confirms the equation of state to be a powerful tool for design and scale-up to full sized field installations having economically advantageous energy requirements.

KPS is now relocating the pilot plant to the Koch Corpus Christi refinery where we will continue operation with a new test program. The future tests will examine column internals for the hydraulic characteristics (load and turn-down as well as efficiency/HETP). It is anticipated that

both trays and packings will be operated. Other separations will be tested for potential commercialization such as those encountered in the production of substitute natural gas and synthesis gas.

KPS plans to keep the pilot plant available during the next several years to support the first full-scale commercial projects. This will permit verification of unit designs or optimization on a much more flexible basis than for a corresponding full-scale unit. The pilot plant will also be available for customer tests as required for particular feeds, product specifications or operating requirements.

APPLICATIONS

The application of the Ryan/Holmes processes to EOR gas processing and high CO₂ natural gases are two examples that illustrate the potential for full scale installation.

Enhanced oil recovery projects

CO₂ injection for enhanced oil recovery (EOR) is an ideal application for the Ryan/Holmes process. Candidate fields for CO₂ flooding typically produce rich associated gas containing small amounts of CO₂. With CO₂ injection, the CO₂ content of the produced gas will increase as CO₂ breaks through in the reservoir. Eventual CO₂ content may reach the 85 to 90% range. The CO₂ will be recycled back to the reservoir to reduce the purchased CO₂ volume. It is desirable to remove NGL's for sales and methane removal may be required. Additionally, any H₂S in the CO₂ must be removed to an acceptable level (usually less than 100 ppm).

A processing facility for such a project must be able to handle a wide range of operating conditions. Table IV shows an example of the range of volumes and compositions which might be encountered on a typical CO₂ project.

TABLE IV.
EOR Gas Production

COMPONENT	Mole %		
	EARLY YEAR	MIDDLE YEAR	PEAK YEAR
N ₂	.24	.09	.07
CO ₂	57.58	81.83	85.97
H ₂ S	.39	.15	.12
C ₁	16.67	6.56	4.95
C ₂	8.64	3.41	2.58
C ₃	7.38	2.96	2.25
iC ₄	1.22	.51	.39
nC ₄	3.39	1.47	1.14
iC ₅	1.01	.57	.40
nC ₅	1.18	.64	.51
C ₆	.84	.61	.53
C ₇ +	1.46	1.20	1.09
MMSCFD	12	59	73

A Ryan/Holmes flow sheet for such an application is shown in Fig. 12. The produced gas after compression

dehydration and chilling is fed to the process at 500 psia. A process sequence similar to Fig. 6 can be used.

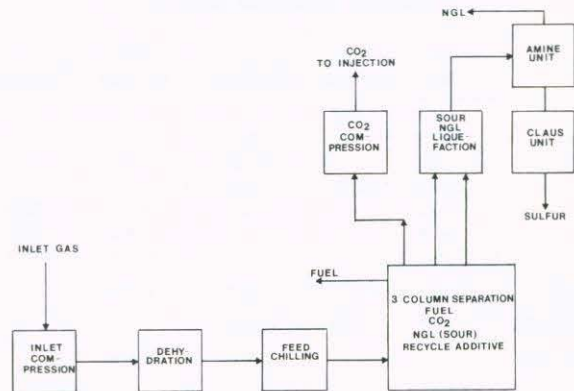


FIG. 12. Ryan/Holmes process—EOR application.

Column 1 separates C₁ and CO₂ producing a sales gas or feed with 2% CO₂. Column 1 condenser operates at about -120°F. The bottoms is fed to the CO₂ column which is operated at 350 psia with an overhead temperature of about 5°F. CO₂ is produced with 50 ppm or less H₂S. The CO₂ column bottoms contain NGL's and additives to be recycled which are separated in the third column. The additive column can usually be designed to use cooling water for its condenser. The NGL product contains practically all the H₂S and the residual CO₂; these are removed in an amine sweetening unit. H₂S can be converted to sulfur in a Claus unit.

Material balances are shown in Table V which shows both an early year and a peak volume year. In the early years, there is extra capacity compared to the peak volume year. The recovery of C₂ and the elimination of H₂S can, therefore, be more thorough. We often find that the equipment is sized for peak year requirements but the project evaluation needs the recoveries and utilities to be evaluated for each year of projected reservoir history.

Due to the low methane content in years of peak CO₂ production, the C₁/CO₂ column can be designed and operated in a different manner. By increasing the volume of recycle additive to the column, the overhead temperature can be raised to -35°F. This modification is attractive in that the column can now be fabricated of carbon steel and the need for cascade refrigeration has been eliminated. In the early years, the methane to CO₂ ratio is much higher. Required recycle volume is much greater than in the -120°F case. But, in the early years, the facility has excess capacity in the Column 3 system. Thus, the recycle volume per Mcf of feed can be increased to make -35°F operation attractive even in the early years.

For some CO₂ projects, the removal of methane is not required or economically attractive. In these cases, Columns 2 and 3 are used for NGL recovery and H₂S removal similar to Fig. 8. The NGL's are handled as in the previous case and the methane is reinjected along with the CO₂.

Naturally occurring high CO₂ gas field

KPS has received a number of inquiries for processing naturally occurring high CO₂ gas fields. In all of these cases, the methane is desired as a purified product stream.

TABLE V.
EOR Gas Separation Material Balances
EARLY YEAR (Moles/Hr.)

	Feed Gas	Fuel Product	CO ₂ Product	NGL Product	% Recovery
N ₂	3.1	3.1	—	—	
CO ₂	739.3	4.2	715.1	20.0	
H ₂ S	5.0	—	5 ppm	5.0	
C ₁	214.2	199.2	15.0	—	
C ₂	110.9	—	8.0	102.9	92.8
C ₃	94.8	.1	.3	94.4	99.6
C ₄ +	116.8	.7	—	116.1	99.4
TOTAL	1284.1	207.3	738.4	338.4	
MMSCFD	11.7	1.89	6.73		
GAL/DAY				93,200	

PEAK YEAR (Moles/Hr.)

	Feed Gas	Fuel Product	CO ₂ Product	NGL Product	% Recovery
N ₂	5.6	5.6	—	—	
CO ₂	6880.5	7.3	6885.5	7.17	
H ₂ S	9.2	—	50 ppm	8.8	
C ₁	396.9	352.2	44.7	—	
C ₂	206.5	—	84.0	122.5	59.3
C ₃	180.0	.2	7.9	171.9	95.5
C ₄ +	324.9	1.3	.4	323.2	99.5
TOTAL	8003.6	366.6	6992.9	644.1	
MMSCFD	72.9	3.34	63.7		
GAL/DAY				196,800	

As stated previously, the Ryan/Holmes technology can produce either a pipeline quality gas (2% CO₂) or an LNG quality gas (less than 100 ppm CO₂).

Some of the applications which we have studied have very remote locations and do not require the production of CO₂ as a salable product. In these cases, the CO₂ can be vented to the atmosphere after expansion and heat exchange. In these cases, often no external refrigeration will be required. (All of the required process refrigeration can be obtained from the CO₂ product.) In cases where the CO₂ is desired as a valuable byproduct, production at 300 to 500 psig by the Ryan/Holmes technology is a substantial economic advantage over solvent processes. This permits direct compression for pipeline or injection purposes or alternatively condensation and sale as liquid product.

Quite often these fields are available at higher pressure than required for the Ryan/Holmes process. Therefore, the feed stream can be expanded to the demethanizer pressure level to produce cold temperatures and to recover some of inherent energy. The process requires two columns along the lines of Fig. 7. In applications where the CO₂ is more than half of the feed stream it is often possible to recompress the product methane stream back to the original feed pressure using the recovered energy from the feed expansion. Table VI sets forth some typical performance data for a 70% CO₂ feed stream.

The integration of the Ryan/Holmes process with an LNG process has significant potential economic benefit. This is because the cold high pressure methane from the demethanizer is suitable for direct feeding to the liquefac-

TABLE VI.
High CO₂ Gas Separation

Basis: Pipeline Sales Gas, 1000 psig, 2% CO₂
Product CO₂ 2000 psig
Feed 2000 psig

Feed:	
C ₁ , MMSCFD	27.
CO ₂ , MMSCFD	73.
Total	100.
Fuel, MMSCFD	4.1
CO₂, MMSCFD	73.4
Sales Gas, MMSCFD	22.5
Power, H.P.	15,800

tion cycle. Table VII gives some comparisons between a typical sweetening and LNG system and the combined integrated Ryan/Holmes LNG system. This comparison assumes that a cascade refrigeration process is used for the LNG production since common stages of refrigeration can be conveniently integrated with the Ryan/Holmes process. However, alternative LNG approaches, such as mixed refrigerant loops, could easily be incorporated as well.

TABLE VII.
Integrated LNG/CO₂ Removal

Basis: LNG Production
Product CO₂ 2000 psig
Feed 2000 psig

Feed	Ryan/Holmes	Physical Solvent
C ₁ MMSCFD	27.	27.
CO ₂ MMSCFD	73.	73.
Total	100.	100.
Fuel MMSCFD	6.1	7.8
CO₂ MMSCFD	73.4	73.4
LNG MMSCFD	20.5	18.8
Power HP, Net	24,000	30,300

In summary, the Ryan/Holmes LNG integration offers substantial savings in power and fuel consumption over a physical absorption process for the same production. This results in more net product being produced.

SUMMARY AND CONCLUSIONS

A method for treating CO₂ and H₂S in gas and oil fields has been developed. KPS's Ryan/Holmes processes use an additive obtained from NGL's which makes possible distillative separation of C₁ from CO₂ and H₂S to produce a gas that satisfies pipeline or LNG feed specifications. The use of additive also permits the separation of CO₂ from C₂ and H₂S to produce CO₂ suitable for pipelining and to obtain good ethane recovery. Verification of the processes for a wide variety of feeds was obtained in the laboratory and by the results of a six-month pilot plant program.

The Ryan/Holmes processes offer flexibility, utilize conventional distillative equipment and do not introduce external chemicals. These processes are projected to be economically attractive in applications such as treatment of gas production from CO₂ injection and treatment of high CO₂, low Btu gases. Atlantic Richfield has concluded the first license agreement with KPS in order to assure that the Ryan/Holmes processes may be utilized full scale in their EOR operation at the Willard unit, Wasson field. KPS has patents issued and pending regarding this technology. The processes are being offered under license for commercial application by KPS.

REFERENCES

1. Cheung, H.; Zander, E. H. "Solubility of Carbon Dioxide and Hydrogen Sulfide in Liquid Hydrocarbons at Cryogenic Temperatures." **Chem. Eng. Progr. Symp. Ser.** No. 88, vol. 64, p. 34, 1968.
2. Davalos, J.; Anderson, W. R.; Phelps, R. E.; Kidnay, A. J. "Liquid-Vapor Equilibria at 250.00 K for Systems Containing Methane, Ethane and Carbon Dioxide." **J. Chem. Eng. Data** **21**, No. 1, p. 81, 1976.
3. Davis, J. A.; Rodewald, N.; Kurata, F. "Solid-Liquid-Vapor Phase Behavior of the Methane-Carbon Dioxide System." **A.I.Ch.E. J.** **8**, No. 4, p. 537, 1962.
4. Donnelly, H. G.; Katz, D. L. "Phase Equilibria in the Carbon Dioxide-Methane System." **Ind. Eng. Chem.** **46**, p. 511, 1954.
5. Jones, J. K. "The Cryogenic Upgrading of Low-Btu Gases Containing Air, Carbon Dioxide and Nitrogen." **Proc. Gas Proc. Assn.**, 1974.
6. Kurata, F. "Solubility of Solid Carbon Dioxide in Pure Light Hydrocarbons and Mixtures of Light Hydrocarbons." **GPA Res. Rep. RR-10**, Feb. 1974.
7. Mraw, S. C.; Hwang, S. C.; Kobayashi, R. "Vapor-Liquid Equilibrium of the CH₄-CO₂ System at Low Temperatures." **J. Chem. Eng. Data** **23**, No. 2, p. 135, 1978.
8. Nagahama, K.; Konishi, H.; Hoshino, D.; Hirata, M. "Binary Vapor-Liquid Equilibria of Carbon Dioxide-Light Hydrocarbons at Low Temperature." **J. Chem. Eng. Data** **7**, No. 5, p. 323, 1974.
9. Pagani, G.; Guerreri, G.; Peri, B. "Method for the Purification of Natural Gas Having a High Content of Acidic Gases." U.S. Pat. 4,097,250, June 27, 1978.
10. Schianni, G. C. "Cryogenic Removal of Carbon Dioxide from Natural Gas." **Inst. Chem. Eng. Symp. Soc.** No. 44, p. 50, 1976.
11. Sobocinski, D. P.; Kurata, F. "Heterogeneous Phase Equilibria of the Hydrogen Sulfide-Carbon Dioxide System." **A.I.Ch.E. J.** **5**, No. 4, p. 545, 1959.
12. Sterner, C. J. "Phase Equilibria in CO₂-Methane Systems." **Adv. Cryo. Eng.** **6**, p. 467, 1961.