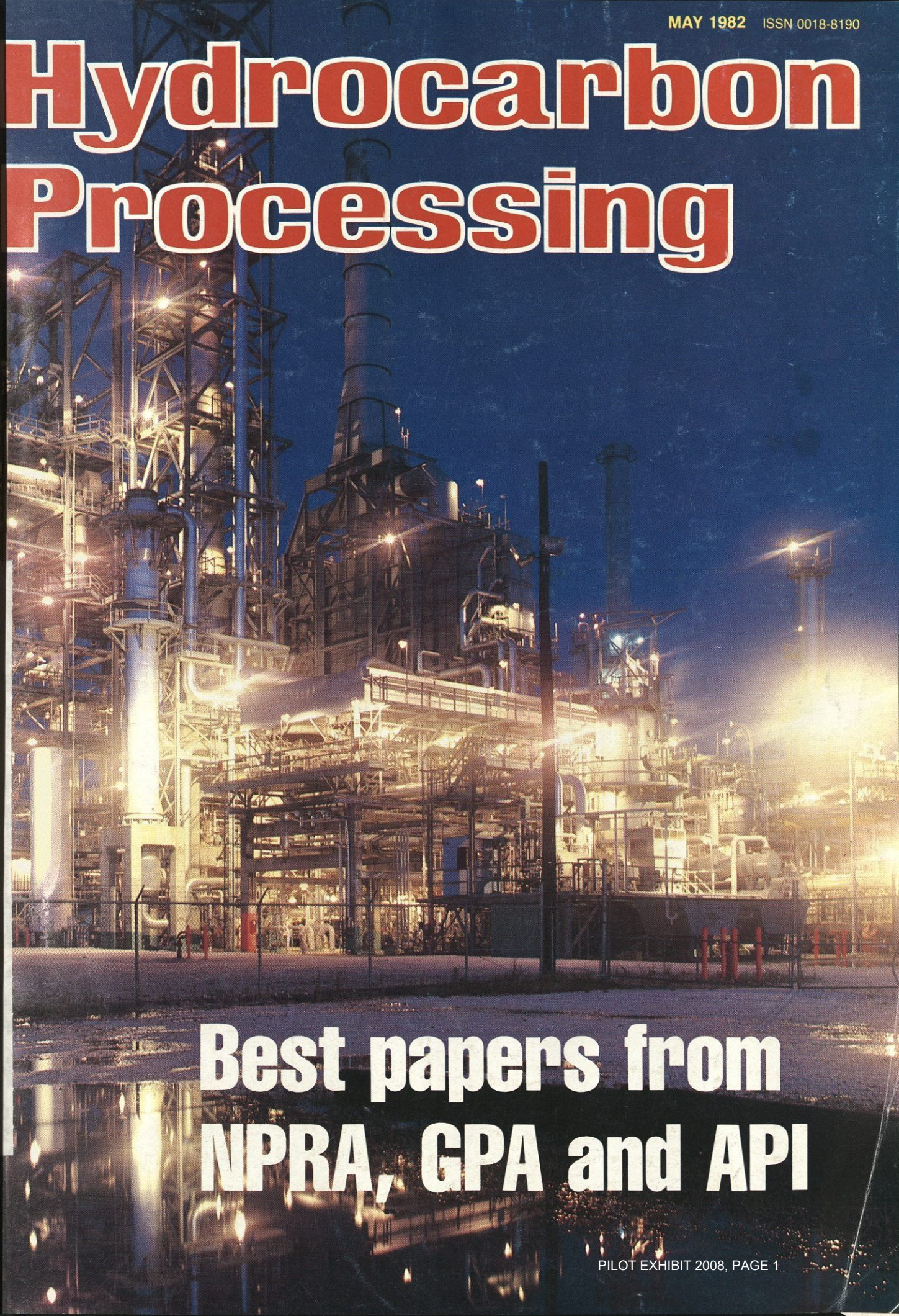


Hydrocarbon Processing

A large industrial refinery at night, illuminated by bright lights, with complex piping and structures. The scene is dominated by tall distillation columns and a dense network of pipes and walkways. The lights create a strong contrast against the dark sky, and the foreground shows a dark, reflective surface, possibly a pool of water or a wet ground, mirroring the industrial structures.

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Process improves acid gas separation

Ryan/Holmes cryogenic processes overcome roadblocks to distillation of C_1 - CO_2 , C_2 - CO_2 and CO_2 - H_2S systems

A. S. Holmes and **J. M. Ryan**, Koch Process Systems, Inc, Westboro, Mass., and **B. C. Price** and **R. E. Styring**, ARCO Oil and Gas Company, Dallas, Texas.

CARBON DIOXIDE SEPARATES CLEANLY from troublesome systems when distillation additives are strategically used. This technique is used in patented Ryan/Holmes Processes for three otherwise now impossible distillations:

- Methane from carbon dioxide
- Carbon dioxide from ethane and heavier liquids
- Carbon dioxide from hydrogen sulfide mixtures.

A number of additives can be used in these processes, but NGL's normally found at plantsite are preferred.

Process performance is technically outstanding since methane is produced directly from a $C_1/CO_2/H_2S$ stream to meet either pipeline specifications or LNG feed requirements, and carbon dioxide suitable for pipelining can be produced with good ethane recovery from a $CO_2/C_2/H_2S$ stream. Process economics and operability show advantages over physical absorption.

Three industrial opportunities now exist:

- Upgrading natural gas containing large amounts of CO_2 and H_2S
- Achieving high NGL recovery in treating hydrocarbon-rich sour gases

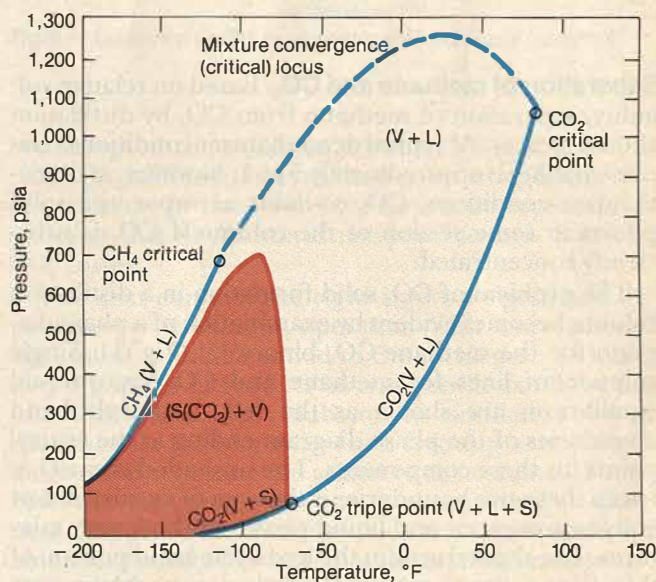


Fig. 1 — Phase diagram, CH_4 - CO_2 binary.

- Processing gases from EOR fields.

Atlantic Richfield has concluded a license agreement to assure that these processes will be used full scale in their EOR operation at the Willard unit, Wasson Field.

THE PROBLEMS

Increasing need to separate methane from carbon dioxide while removing hydrogen sulfide occurs in several situations, including gas treatment at fields using enhanced oil recovery by carbon dioxide miscible flooding. In other operations, it is necessary to separate ethane from carbon dioxide. These separations have inherently difficult characteristics that make simple distillation unacceptable.

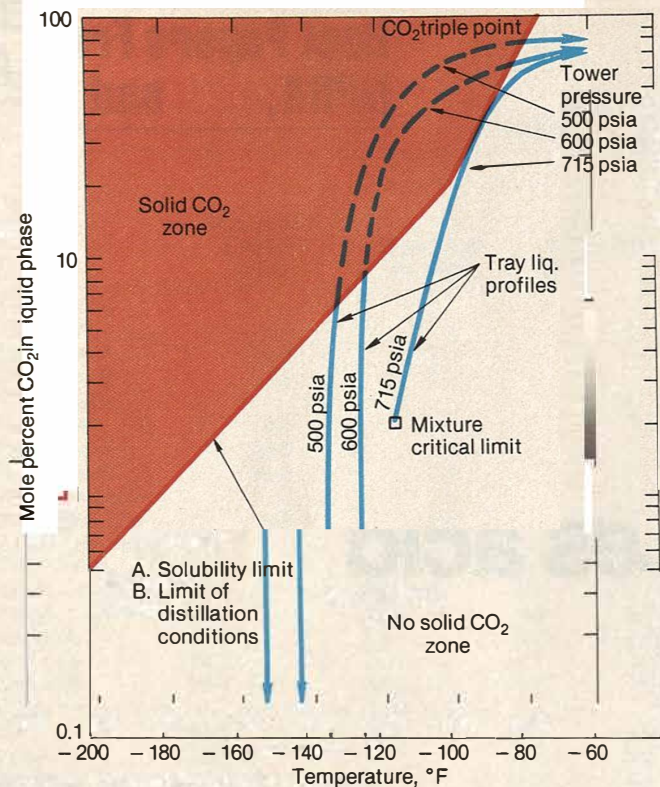


Fig. 2 — Distillation profile, CH₄-CO₂ binary.

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

The problem of CO₂ solid formation in a distillation column becomes evident by examination of a phase diagram for the methane-CO₂ binary^{1,2,3,4} (Fig. 1). 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 phases in equilibrium consist of a binary vapor and solid CO₂. Operation here has solid CO₂ present.

Because the tip of this area extends to a higher pressure (approximately 705 psia) than the critical pressure of methane, there is no way to go from a composition of high CO₂ to pure methane at constant pressure without passing through this solid region. A number of combinations of single and double column systems^{5,6,7} operating at different pressures have been proposed. However, these schemes involve operation close to the methane critical, or methane-CO₂ mixtures critical or to CO₂ freezing conditions. They also require high energy use and capital. Therefore, they are uneconomic compared to other CO₂ removal systems.

Figure 2 shows the solid barrier as solubility limits of solid CO₂ in CO₂-methane liquid mixtures. The line extending diagonally across the figure represents the sol-

ubility limit of CO₂. Left of and above this line, solid CO₂ is formed. Conversely, below and to the right, vapor-liquid equilibrium exists and no solid formation is observed. The curved lines show 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. Their conditions exceed solubility limit. The column will freeze here.

Unless operation is above 705 psia (the tip of the solid CO₂ boundary, Fig. 1), distillation will always pass through the solids formation to go from a high CO₂ mixture to pure methane. Operation at 715 psia could avoid solid CO₂ formation, however, the limit on methane 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.

Separation of CO₂ from C₂⁺ hydrocarbons. Distillation of ethane from CO₂ is limited by formation of an azeotrope at an approximate composition of 67% CO₂ and 33% ethane.^{8,9} This azeotrope does not significantly change in composition with different operating pressures (Fig. 3), therefore, distillations from either side of the azeotrope is limited by the azeotrope composition.

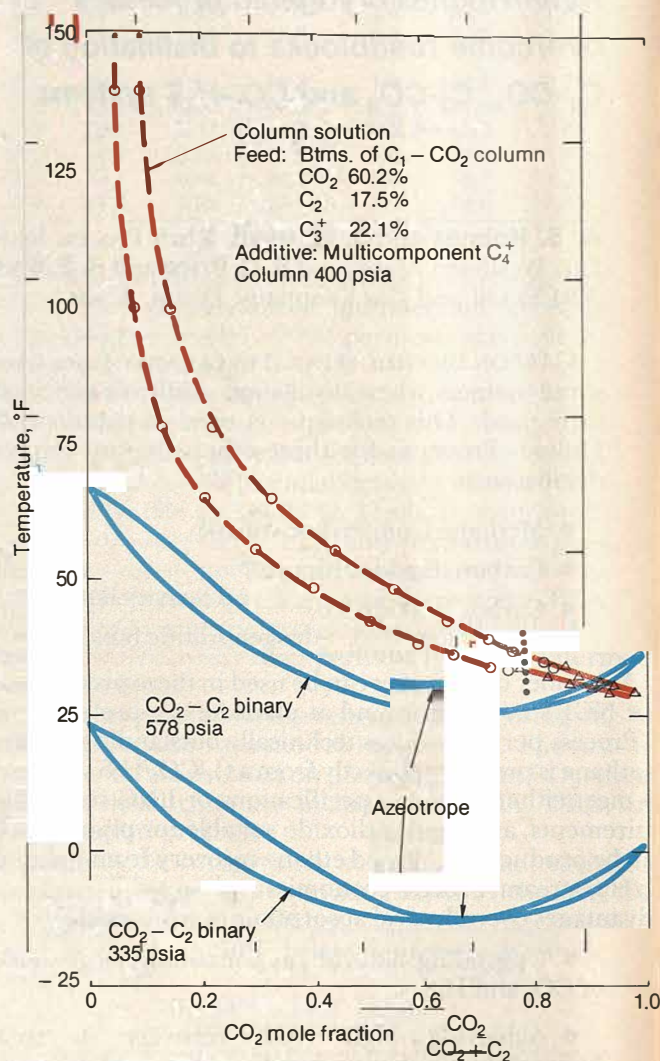


Fig. 3 — Vapor-liquid equilibria, CO₂-C₂.

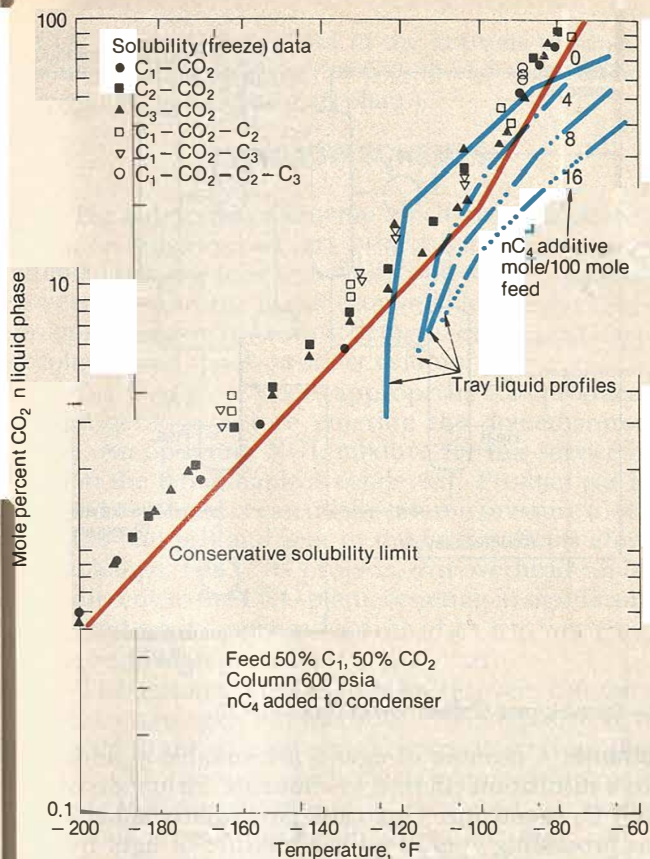


Fig. 4 — Distillation profile, binary feed with nC_4 additive.

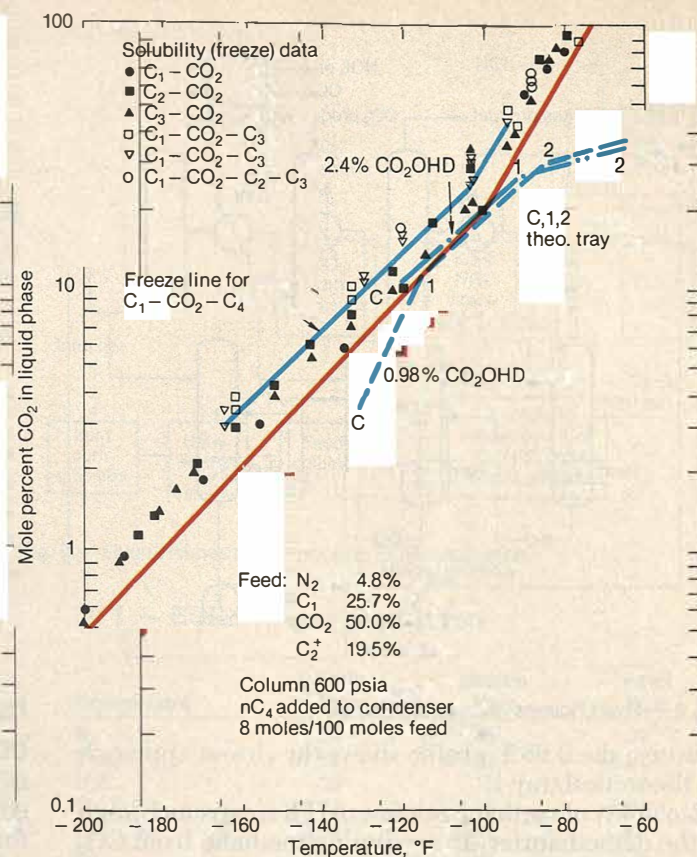


Fig. 5 — Distillation profile, multicomponent feed with nC_4 additive.

In cases where feed contains substantial quantities of ethane, it is often desirable to recover ethane with the other NGL components as a salable product. A plot of the vapor-liquid equilibria of a typical bottoms composition from the demethanizer column (dotted line, Fig. 3) shows that a pure CO_2 bottoms product could be made from the distillation column but that the overhead product would be limited to the azeotrope composition which would contain essentially all the ethane.

Separation of CO_2 and H_2S . In the separation of CO_2 from H_2S , distillation is difficult because the relative volatility between the substances is quite small. While an azeotrope between CO_2 and H_2S does not exist, vapor-liquid equilibrium approaches azeotrope character at high CO_2 concentrations.¹⁰

RYAN/HOLMES APPROACH

The Ryan/Holmes approach to these distillations is to add a suitable agent to the distillation in order to significantly alter the system. These additives are normally simple mixtures of C_3^+ hydrocarbons, which are obtained by distillation and separation from the feed mixture itself.

Methane- CO_2 . An example is a Ryan/Holmes demethanizer column with a pure n -butane additive, (Fig. 4). The solid diagonal line (Fig. 4) is the most conservative boundary that can be drawn from all of the available data on CO_2 solubility.^{11,12} The solid tray profile line shows a binary C_1 - CO_2 distillation without additive producing a methane top product containing 2% CO_2 and a

bottoms product containing less than 1% methane. Operating conditions of this column pass through a significant portion of the solid CO_2 formation region. This indicates that distillation is not possible and that solid CO_2 forms.

The next curve to the right shows a significant improvement in column operation with only a small amount of n -butane added to the condenser. (4 moles per 100 moles of feed.) 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 which sets a corresponding amount of additive to be fed to the top of the column.

Figure 5 goes a step further in illustrating the role of additive for avoiding freezing. The actual freeze line is drawn to the left and above the most conservative freeze line that we had before. This actual freeze line is based on data for certain applicable ternary systems of methane, CO_2 and n -butane.¹² This illustrates the beneficial shift for multicomponent systems which include C_2^+ hydrocarbons in addition to methane and CO_2 .

Other NGL hydrocarbons demonstrate similar behavior. Tray profiles (Fig. 5) 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

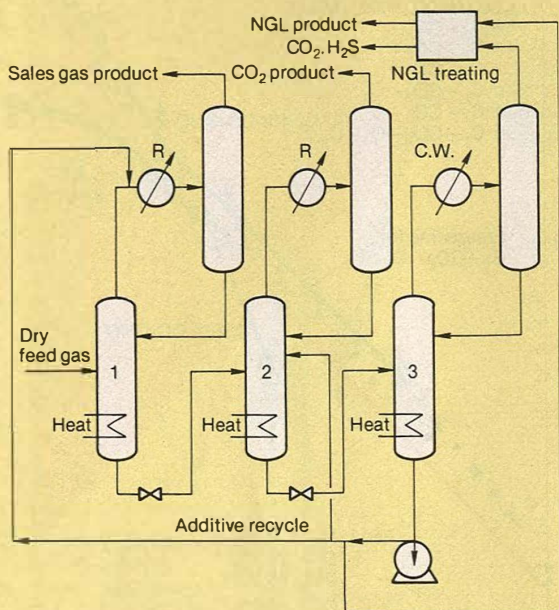


Fig. 6 — Ryan/Holmes process, EOR plant.

contrast, the 0.98% profile shows the closest approach on theoretical tray 1.

Volatility of methane relative to H_2S is extremely high in the demethanizer. In separating methane from CO_2 to normal pipeline quality ($<2\%$ 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:

- Additives significantly raise operating temperatures which lowers refrigeration requirements.
- Additives increase the methane/ CO_2 relative volatility above that for the binary system.
- Additives permit higher pressure operation.

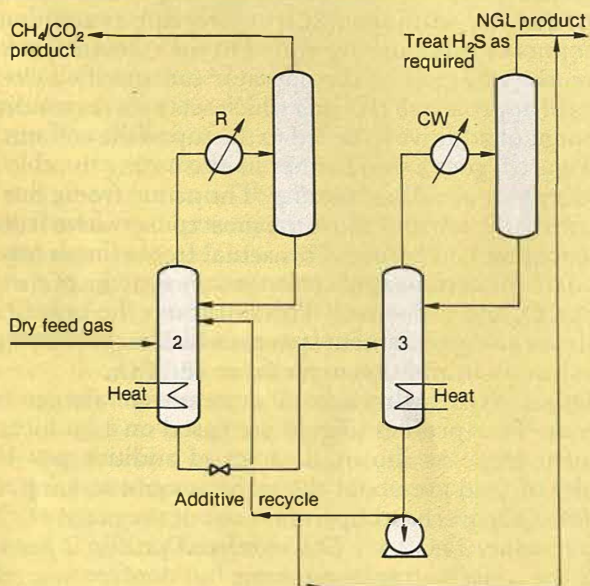


Fig. 8 — Ryan/Holmes process, combined CH_4/CO_2 product.

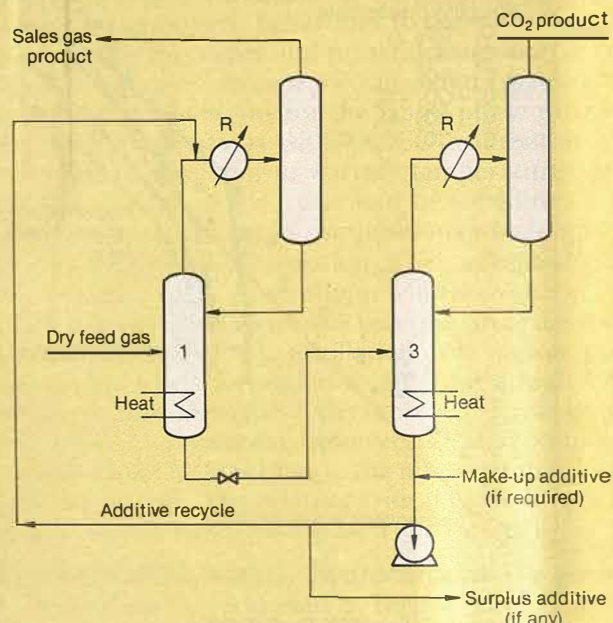


Fig. 7 — Ryan/Holmes process, low Btu gas (no H_2S).

CO_2 -ethane. A number of agents are suitable as additives to a distillation column to eliminate formation of ethane- CO_2 azeotrope. One class particularly suitable for gas processing operations is a mixture of light hydrocarbons such as butanes and heavier hydrocarbons. The upper dashed phase envelope (Fig. 3) indicates the behavior of a multicomponent feed distilled with a multicomponent C_4^+ additive plotted on a CO_2 -ethane pseudo-binary basis. All ranges of composition from 0 to 100% CO_2 can be achieved in this mode of distillation. Volatility of CO_2 to ethane remains above 1.0, and the azeotrope is circumvented.

The top portion of the column above the additive introduction tray represents a knockback zone to reduce the concentration of additive in the CO_2 product. Immediately above the additive introduction point the relative volatility reverses (i.e., CO_2/C_2 volatility <1).

The same additive compositions that are effective for demethanizer operation can be used for CO_2 -ethane.

H_2S . When H_2S is present it must be thoroughly removed from all product streams. Typical sales gas specifications require $<1/4$ grain of H_2S per 100 cu ft and typical carbon dioxide specifications require <100 ppm H_2S in CO_2 product. Finally, H_2S is normally converted to elemental sulfur by the Claus process where feeds are practically limited to a molar ratio of CO_2 to H_2S of no more than 3 to 1. These required separations can be accomplished by the Ryan/Holmes processes.

Improved separation is obtained by the addition of n-butane (or other suitable additives) to the system.

In the presence of additive, the column separating CO_2 and ethane also benefits from a significant enhancement in the separation of H_2S from CO_2 . This allows carbon dioxide to be produced at substantially less cost than would be otherwise possible without additive present. In fact, the carbon dioxide column can be operated to meet three separate criteria:

- Purity of CO_2 with respect to ethane and H_2S .
- Recovery of ethane and higher hydrocarbons

• CO₂ to H₂S ratio control in the bottoms product. (This ultimately is the ratio of CO₂ to H₂S that will be removed and fed to the Claus plant.)

TYPICAL FLOW SCHEMES

Fig. 6 describes a flow scheme which that can be used for an enhanced oil recovery project (i.e., varying CO₂ content in the feed and high NGL content which is to be recovered to the maximum economic level). This system consists of three columns: demethanizer, CO₂ product column, and NGL product column.

Dry feed is cooled by both appropriate cold products and refrigeration before entering the demethanizer column. An optimum NGL mixture for this service is added in the demethanizer condenser. Product gas is produced overhead at essentially column pressure (normally 450-650 psi) and sent to the battery limits after heat exchange. For LNG projects, this overhead could be fed directly to the LNG plant, resulting in significant energy and capital savings because of its low temperature and high pressure.

The bottoms is fed to the CO₂ recovery column after heat exchange. The additive NGL mixture is introduced to the column several trays down from the top. The CO₂ product which meets required hydrocarbon and H₂S specifications, is produced at essentially column pressure (normally 350 to 550 psig).

Bottoms product is fed to NGL recovery. CO₂ has been stripped to the required ratio of CO₂ to H₂S. A light hydrocarbon is produced overhead which contains all the H₂S and CO₂ fed to the column. A bottom stream is suitable for use as an additive. A slip stream, taken from the bottom to remove the net C₄⁺ contained in feed, is mixed with net overhead for NGL product.

The NGL product can be treated either as a liquid or vapor by an amine system to remove the acid gas content. This sweetening step is significantly less expensive than original feed treatment would have been. Separated acid gases can be fed directly to a Claus plant.

Many other combinations of Ryan/Holmes distillations can be envisioned. Each must be evaluated as to optimum configuration. Some variations are:

• A scheme for processing a naturally occurring lean gas when H₂S is not present (Fig. 7). Only two columns are required, the second being an additive recovery column which operates as a conventional distillation. This is the least expensive configuration for the process.

• A process where methane-CO₂ separation is not required (Fig. 8). This applies where combined methane-CO₂ overhead can either be reinjected, burned directly as low Btu fuel, further distilled conventionally to produce a 7-800 Btu methane fraction, or by Ryan/Holmes distillation to produce a higher purity methane. Ethane and heavier hydrocarbons are recovered in the bottoms and processed in the additive recovery column.

APPLICATIONS

Application of the 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. Candidate fields for CO₂ flooding typically produce rich

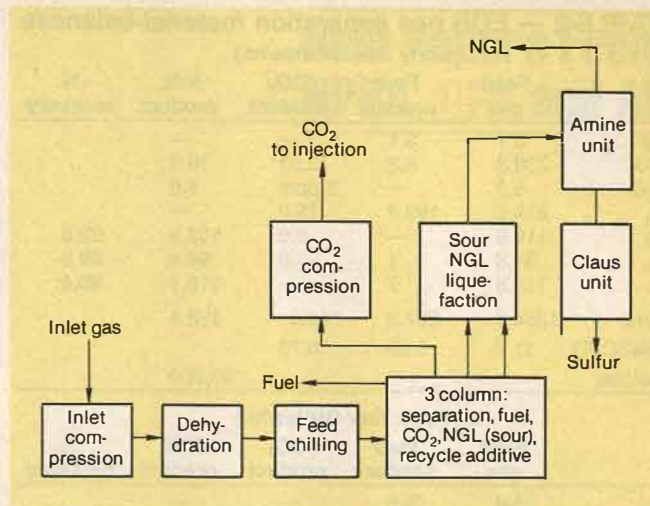


Fig. 9 — Ryan/Holmes process, EOR application.

TABLE 1 — EOR gas production
Mole %

Component	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

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 to reduce the purchased CO₂ volume. It is desirable to remove NGLs 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 1 shows an example of what might be encountered on a typical CO₂ project.

A flow sheet for such an application is shown in Fig. 9. Produced gas after compression, dehydration and chilling is fed at 500 psia. A process sequence similar to Fig. 6 can be used.

Column 1 separates C₁ and CO₂ producing a sales gas or fuel 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 NGLs 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.

TABLE 2 — 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	72.51	10.0	
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	748.4	328.4	
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	6855.5	17.7	
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	

TABLE 3 — 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
CO ₂ , MMSCFD	73.4
Sales gas, MMSCFD	22.5
Power, H.P.	15,800

TABLE 4 — 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
CO ₂ MMSCFD	73.4	73.4
LNG MMSCFD	20.5	18.8
Power HP, net	24,000	30,300

Material balances (Table 2) show both an early year and a peak volume year. In the early years, there is extra capacity compared to the peak volume year. Recovery of C₂ and elimination of H₂S can, therefore, be more thorough. Equipment is sized for peak year requirements but project evaluation needs recoveries and utilities to be evaluated for each year of reservoir use.

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 volume of recycle additive to the column, the overhead temperature can be raised to -35 °F. This allows the column to be fabricated of carbon steel and eliminates need for

cascade refrigeration. In the early years, 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, 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. Methane is desired as a purified product stream where CO₂ occurs naturally in high concentrations in a gas field. In these cases either a pipe line quality gas (2% CO₂) or an LNG quality gas (less than 100 ppm CO₂) can be produced.

Some applications have very remote locations and do not require production of CO₂, as a salable product. In these cases, CO₂ can be vented to the atmosphere after expansion and heat exchange. Often no external refrigeration is required. In cases where CO₂ is a valuable byproduct, production at 300 to 500 psig is a substantial economic advantage over solvent processes. This permits direct compression for pipeline or injection purposes or alternatively condensation and sale.

When field pressure is higher than required for the process, 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 CO₂ is more than half of the feed stream it is often possible to recompress product methane stream to feed pressure using recovered energy from feed expansion. Table 3 sets forth some typical performance data for a 70% CO₂ feed stream.

Integration of the Ryan/Holmes process for LNG has significant potential economic benefit because cold high pressure methane from the demethanizer is suitable for direct feeding to the liquefaction cycle. Table 4 compares a typical sweetening and LNG system and the combined integrated Ryan/Holmes LNG system. This assumes that a cascade refrigeration process is used for the LNG production, however, alternative LNG approaches, such as mixed refrigerant loops, could easily be incorporated.

ACKNOWLEDGMENT

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