

WEEK OF JULY 18, 1983
A PennWell Publication

OIL & GAS JOURNAL



1200172421 0718832 40 062584
RONALD L SCHEDEL
FLUOR ENGRS & CONSRCT INC
BOX C-11944
SANTA ANA CA 92711
976

GAS PROCESSING REPORT: Plants multiply, but throughput falls, p. 71

U.S. research aims at cheaper drilling, improved oil recovery, p. 41
India going it alone in exploration and development programs, p. 50
Linear programming offers way to optimize pipeline analysis, p. 135
Pakistan's Makran region seen highly prospective exploration area, p. 171

Process can efficiently treat gases associated

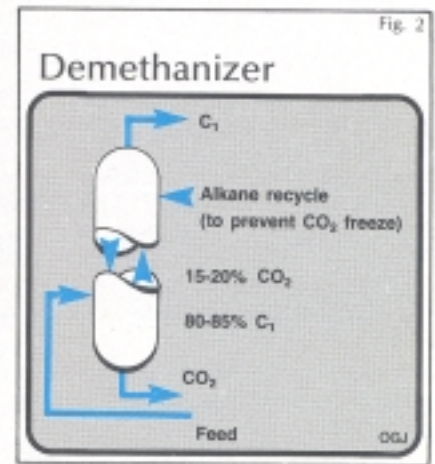
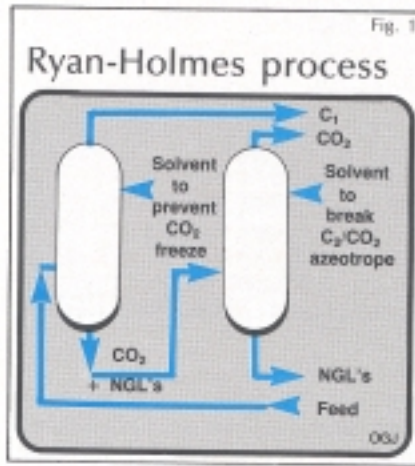
Ronald Schendel
Fluor Engineers
Inc. Irvine, Calif.

Until now, membrane and distillation process alternatives for treating high-CO₂ streams have been viewed as being in direct competition. While membrane processing is commonly linked with conventional processing, amine or hot pot (potassium carbonate) treating for example, the combination of membranes and distillation techniques has not been addressed. One obvious combination would be the use of membranes for bulk separation prior to distillation separation, to improve turn-down capability, and phasing capital requirements for the project.

Amines and hot pot treating involve reaction with the CO₂. They become too energy-intensive when the CO₂ concentration goes beyond 15 or 20%.

Membranes, on the other hand, use partial pressure as the driving force and are most effective at very high concentrations of CO₂. In order to reduce the CO₂ concentration to low enough values for the economical use

Adapted from a presentation made at the Gas Conditioning Conference, University of Oklahoma, Norman, OK., Mar. 7-9, 1983, and one to be made at the American Institute of Chemical Engineers Summer National Meeting, Denver, Colo., Aug. 28-31, 1983.



of amines or hot pot, and still produce a CO₂ stream suitable for reinjection, staging of membranes and costly recompression of a recycle stream are necessary.

Also, the second stage of membranes requires an excessive amount of membrane area/mole of CO₂ produced, particularly when compared with the first section. This is due to the reduced partial pressure of CO₂ which results in a reduced driving force.

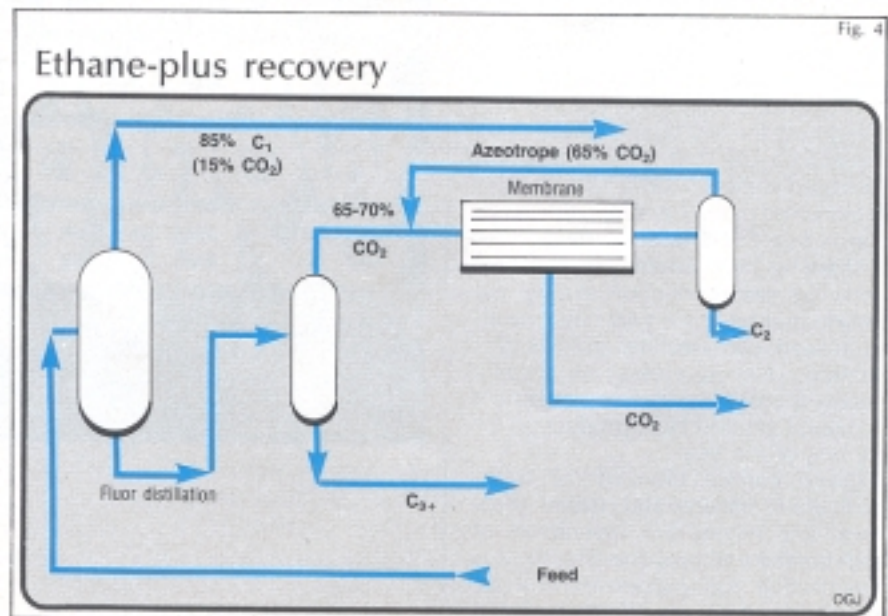
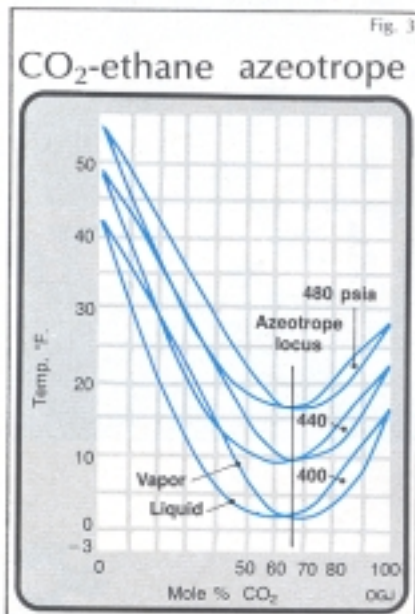
The increased concentration of hydrocarbons results in unacceptable hydrocarbon concentration in the permeate which must be recycled. This requires more membrane area in the first stage as well as recompression

horsepower.

Physical solvents are not suitable because of the high, heavy hydrocarbon content.

Distillation techniques, on the other hand, are economical at higher levels. Use of single-stage membranes, coupled with distillation techniques, should prove advantageous - certainly if the staging of capital requirements allowed by the use of membranes is taken into account.

As an indication of the interest in these processes, we need only look at the active commercial CO₂ flood projects to realize their viability. The Sacroc project, which is the only commercial CO₂ flood project with a





with CO₂ miscible flood

track record, has been operational since 1972. The operators are presently pilot-testing the use of membranes, upstream of hot pot systems, for bulk removal and enhancement of the project economics.

There are two major pipelines completed or under construction to deliver large quantities of CO₂ to West Texas for enhanced oil recovery. One pipeline, built by ARCO, Exxon, and Amerada Hess, will bring 500 MMscfd of naturally occurring carbon dioxide from Colorado and New Mexico. Cynara has been awarded a contract for the upstream processing using Dow membranes.

Shell has also announced its Cortex Pipeline, which will bring CO₂ into the West Texas area. Amoco will either construct a third pipeline or participate in one of the others.

Amoco sees significant economic advantage in the use of membranes. ARCO and Amerada Hess, on the other hand, have both announced their decisions to use the Ryan-Holmes process for processing the associated gas from the CO₂ floods at the Willard unit, and Amerada Hess at its Seminole unit.

Another alternative. There is another area where the use of membranes in combination with distillation techniques may **provide a further advantage**.

Let's examine the Ryan-Holmes process a little more closely (Fig. 1). In the first distillation column, methane is produced as the overhead product. CO₂ plus ethane and heavier hydrocarbons are produced as the bottoms product.

Since CO₂ would normally freeze at the temperatures encountered in a demethanizer, alkane is fed to the top of this column, which effectively prevents the CO₂ freeze-up. The amount of alkane required is moderate, on the order of 10% of the methane produced.

The first column used to separate methane from CO₂ and heavier hydrocarbons may be considered as a condensate stripper, plus a rectifying section where prevention of CO₂ freezeout is required (Fig. 2). The feed temperature is maintained above the freeze point (approx. -80° F.).

The overhead product of the strip

per section consists primarily of methane but still contains 15-20% CO₂. Under some circumstances, particularly where a gas treating facility already exists, it may be desirable to eliminate the rectifier section and remove this relatively small amount of CO₂ by conventional means.

One must compare the economics of providing reflux plus the required alkane recycle in the rectifying section against the operation of a physical solvent, amine, or hot pot plant. The choice is not obvious.

It is important to realize that at this point we have not separated the CO₂ from the hydrocarbons. We have merely removed one of the hydrocarbon components, methane. CO₂ is separated from the remaining hydrocarbons in the second distillation column. Unfortunately, ethane and CO₂ form an azeotrope with an approximate composition of 65% CO₂, 35%

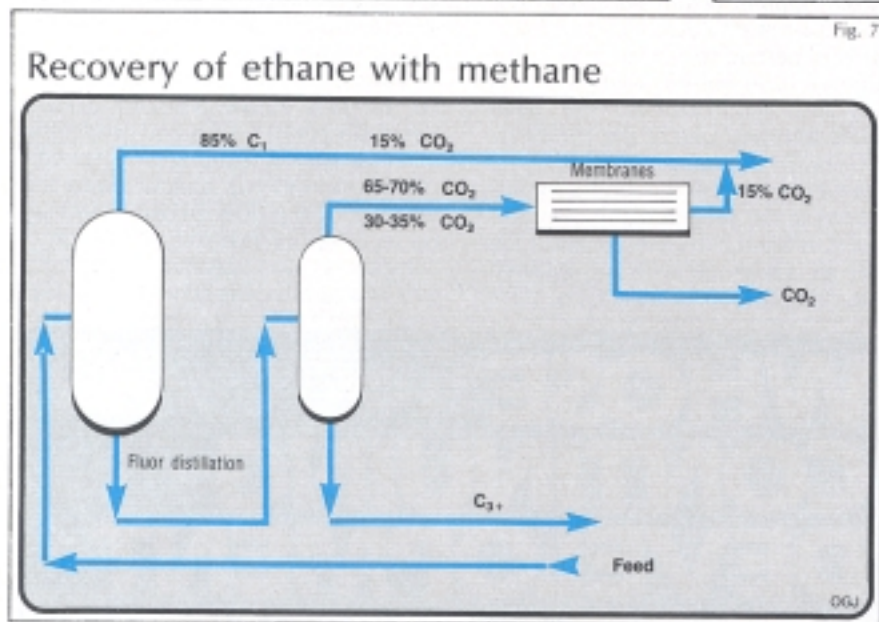
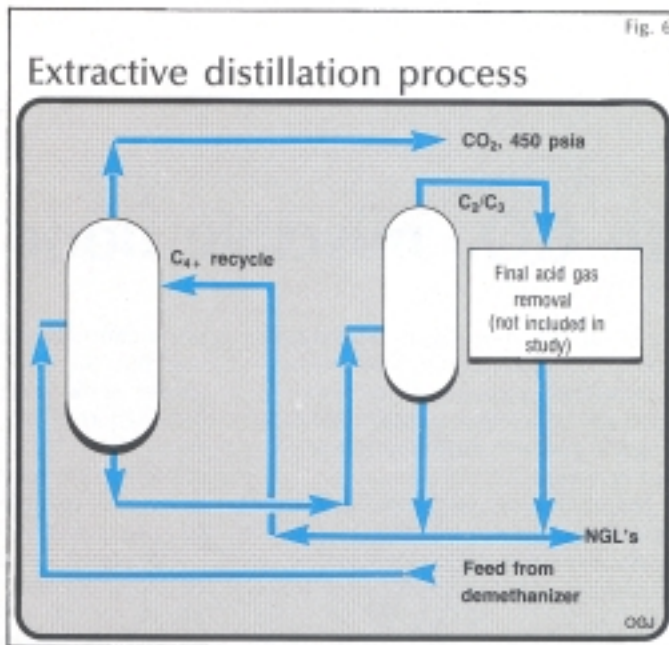
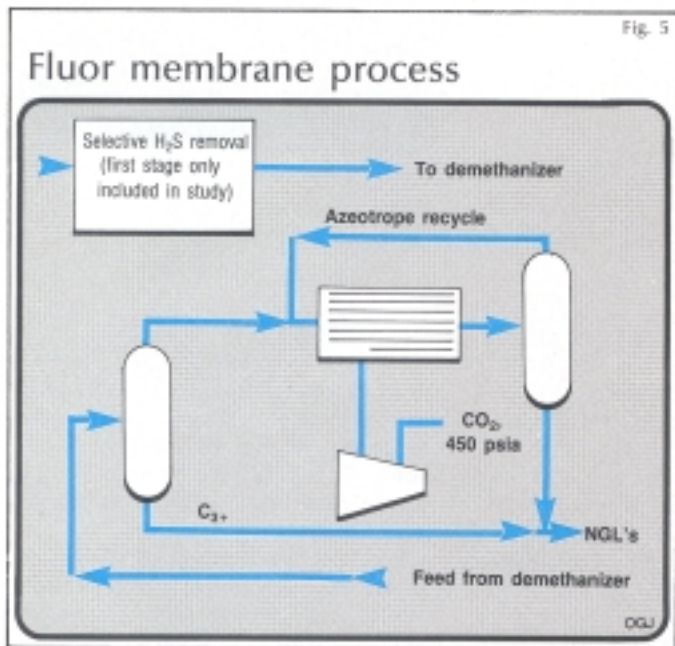
ethane (Fig. 3).

In order to produce CO₂ without the total loss of ethane, an extractive distillation is necessary. Again, the use of an alkane, or mixture of alkanes, is suitable for maintaining a relative volatility for CO₂ over ethane greater than 1.

However, the amount of alkane required is substantial. The actual amount will vary with the ethane extraction desired and the amount of acid gas allowed to exit in the bottoms stream for subsequent removal by amine treating.

Using an ambient temperature lean oil for 90% ethane recovery from a feed with 30-50% CO, and producing an NGL stream meeting CO₂ specifications directly, up to four times the moles of CO₂ produced overhead may be required for lean oil circulation.

By using a refrigerated oil (30° F., 272 K) and allowing some CO₂ (equal



to 5% of the ethane) to be removed by a down-stream amine unit, 80% recovery of ethane is attainable with a lean oil circulation rate of approximately 21/2 times the CO₂ produced overhead. Reducing the ethane recovery further to only 50% and allowing CO₂ equal to 20% of the ethane out of the bottom of the column results in a lean oil circulation of 1 to 1 1/2 times the CO₂ produced overhead. However, the process still requires significant expenditure of energy for the recovery of ethane and heavier hydrocarbons.

An alternate method of processing is to intentionally allow the CO₂ to carry the ethane with it and then separate these components by a nondistillative technique. For example, a physical solvent might be used.

However, this is an ideal application for membranes. It is the heart of a new process developed and patented by Fluor (Fig. 4).

The mixture of carbon dioxide and ethane is produced at pressure and with a high concentration of CO₂, so we have the required driving force.

* The mixture is the overhead product of a distillation column and is therefore very clean. No pretreatment is required; in most **membrane applications** the pretreatment may be extensive and costly.

This stream is free of methane. In commercial membranes available today, the separation of CO₂ from ethane and heavier hydrocarbons is much easier than the separation of CO₂ from methane. Separex gives the following separation factors: CO₂ over methane 22-26, CO₂ over ethane 44-52.

In a single pass, a mixture of 70% CO₂ and 30% ethane can produce a CO₂ stream with less than 5% hydro

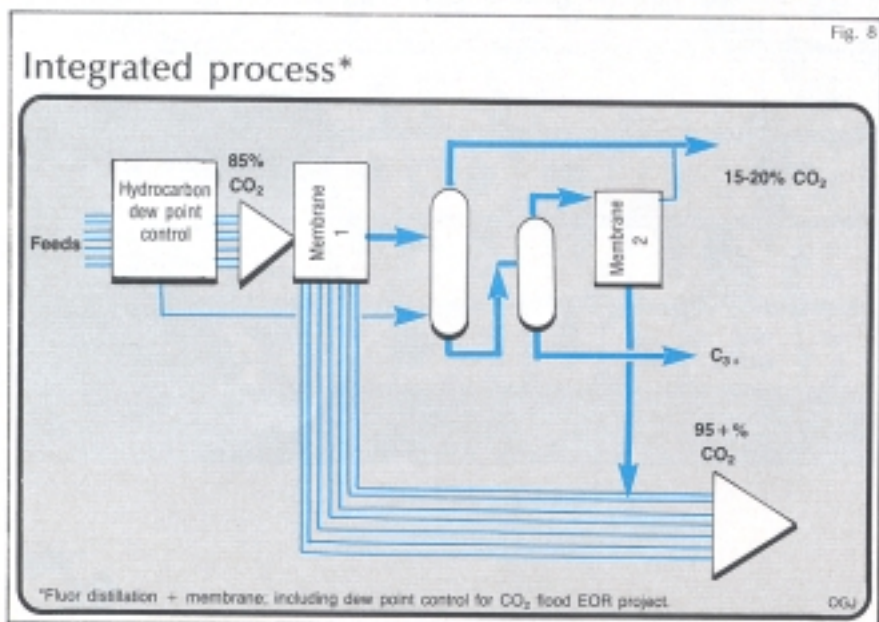


Table 1

Feed composition*

	Mols/hr	Mole fraction
Methane	5.8	0.005
Ethane	254.3	0.218
Carbon	555.9	0.475
Propane	219.3	0.188
i-Butane	25.7	0.022
n-Butane	68.1	0.058
i-Pentane	16.6	0.014
n-Pentane	13.9	0.012
n-Hexane	9.5	0.008
Total	1,169.1	1.000

*Demethanizer bottoms: volume 10.6 MMscfd; temp 60° F.; pressure 590 psia. Hydrogen sulfide, 11.0 mols/hr, is removed by upstream MDEA treating in membrane case.

carbon. The residual hydrocarbon stream will contain approximately 15% CO₂

To produce a CO₂-free ethane, fractionation can again be employed with ethane recovered as the bottoms product. The overhead product again has a composition close to the ethane/CO₂ azeotrope, which is recycled to the membrane unit.

Process comparison. To test the merits of this process, a stream (Table 1) which is the bottoms product of a distillation step is processed to remove methane and yield equivalent products by two different schemes. With the Fluor membrane process (Fig. 5), the methane-free stream is distilled to yield Mostly CO₂ and ethane overhead, with a propane-plus stream as the bottoms product. The ethane produced in the second column is combined with the C₃₊ stream to give a combined NGL stream. The CO₂ is compressed to 450 psi (3.1 X 10⁶ Pa).

In the case of the extractive distillation-type process (Fig. 6), a C₄₊ stream is used to absorb ethane and produce CO₂ as the overhead product. An overhead condenser prevents loss Of C₄ + components with the CO₂ in a typical extractive distillation column.

The bottoms product is sent to the next distillation column where an ethane/propane mix is separated from the C₄₊ stream. The C₄₊ stream is recycled except for a product bleed stream. The ethane/propane mix is sent to an amine unit for final removal of acid gas.

Thus far, the question of H₂S removal has not been addressed. The extractive distillation technique also concentrates the H₂S in the C₂₊ hydrocarbon stream and is removed with the remaining CO₂ in the amine plant. The amount of H₂S present will limit the amount Of CO₂ which can be allowed to leave in the bottoms

Table 2

Utility consumption

Process	HP	Steam, MMBTU/hr	Membrane replacement,\$	Total annual cost, \$million*
Extractive distillation	650	24.7	—	1.34
Distillation-membrane (including H ₂ S removal)	1,190	11.8	98,000	1.08

*Based on \$0.07/kw-hr and \$5/MMBTU

stream and still produce a good Claus feed. In the Fluor process, if H₂S is present it will split, with some going with the CO₂ and some going with the hydrocarbons.

Therefore, it may be advantageous to remove the H₂S prior to distillation. MDEA is a selective amine well suited for this purpose and is used in the Fluor case study.

Two stages of MDEA treating are required. The second stage of MDEA produces an acid gas stream suitable for feed to a Claus plant and is approximately equivalent to the amine plant required in the extractive distillation case.

Therefore, both the second stage of MDEA treating in the membrane distillation case and the amine treating in the extractive distillation case have been eliminated from the study. The first stage of MDEA treating is includ

ed in the Fluor membrane distillation case.

Membrane performance and replacement costs are based on information supplied by Separex with an assumed life of three years. Utility consumption for the first stage of MDEA is provided by Union Carbide for its UCAR HS process used to remove 0.5% H₂S in the feed gas to the demethanizer (approx. 22.4 MMscfd, 0.63x1 06 M3 /day, 30% CO₂). The second stage of MDEA is approximately equivalent to the amine plant in the extractive distillation case, and both have been eliminated from the comparison.

Table 2 compares the utility requirements for both schemes. Horsepower requirements include compressors, pumps, refrigeration horsepower, and air-cooler fans.

Table 3 gives installed capital costs

Table 3

Installed costs

	\$million
Extractive distillation	5.65
Distillation-membrane (including H ₂ S removal)	4.12

for the extractive distillation case and Fluor's membrane case.

The savings in both operating and capital costs, using the Fluor process to break the C₀₂/C₂ azeotrope, are sufficient to pay for H₂S removal at the front end and still realize a net savings of approximately 20% in utilities and over 25% in capital.

Where a bulk stripper plus conventional processing is chosen over RyanHolmes distillation to provide the required methane purity, even greater flexibility is enjoyed by the use of membranes to break the C₀₂/ethane azeotrope (Fig. 7). It is possible to take the residual hydrocarbon stream from the membrane separation, which consists of approximately 85% ethane and 15% C₀₂, and mix this stream with the stripper overhead prior to treating.

This permits economical ethane rejection. With an improved market in ethane, a separate amine contactor or distillation step to recover ethane can be added or reactivated quite easily. Considering the present state of the ethane market and the uncertain future, this flexibility is a very attractive feature.

The cases for comparison were intentionally based on a feed gas to the demethanizer with approximately 30% C₀₂. Any feed gas with a higher concentration of C₀₂ can be effectively processed by a single stage of membranes economically and without the need for recycle to reduce the C₀₂ concentration.

In an integrated scheme (Fig. 8) using membranes and distillation to process associated gas from a C₀₂ flood project, the first membrane section does the bulk C₀₂ removal where membranes are most efficient. The residual gas from this membrane section is remarkably consistent in composition and flow rate throughout the life of the project.

The remainder of the plant can be designed efficiently with low turndown ratio requirements. In one case examined, the maximum flow rate leaving the first membrane stage was approximately three times the flow rate before C₀₂ injection was initiated. This is obviously easier and more economical to design for than a 10 or 20-fold increase in volume.

During one of the later years of the

The authors . . .



Schendel

acid-gas removal, sulfur production, and enhanced oil recovery. Schendel has both BS and MS degrees from Cornell University and is a registered professional engineer in California.

Ronald Schendel is a principal engineer in the technology division of Fluor Engineers Inc. He has specialized in gas processing since joining Fluor in 1975, developing new processes and conducting studies in

project, the feed gas is forecast to have a composition of 85% C₀₂. Over 90% of the C₀₂ in this feed is produced in the first membrane section. The residual gas, ready to process for hydrocarbon recovery, is only 12% of the feed volume. This membrane section can be phased in incrementally due to the modular nature of membranes.

Feed gas in this scheme is cooled down and reheated to prevent heavy hydrocarbons from condensing in the membrane elements. The liquid produced contains heavy hydrocarbons but also considerable C₀₂. This liquid is easily processed with the residual gas from the membranes in the distillation step which follows, for efficient recovery of hydrocarbons.

For the same 85% C₀₂ feed case, 93% of the C₃₊ hydrocarbons are recovered with this scheme based on an actual design using Separex membranes. This scheme is applicable to all membranes available today; however, the Separex membranes claim a higher selectivity which improves hydrocarbon recovery.

On the other hand, other membranes also have unique advantages. For example, Monsanto claims higher operating temperatures, reducing hydrocarbon dew point control requirements.

Since water vapor permeates membranes readily, moderate dehydration upstream of the first membrane section, to meet water specs for the C₀₂, will give a dry gas suitable for distillation.

H₂S removal can be carried out at various stages as required, such as upstream of the first membrane stage for complete sulfur recovery or on the residue gas and NGL stream in situations where H₂S can be reinjected with C₀₂. Other locations would be suitable, depending on final gas treating, fuel gas requirements, liquid hydrocarbon products produced, etc.