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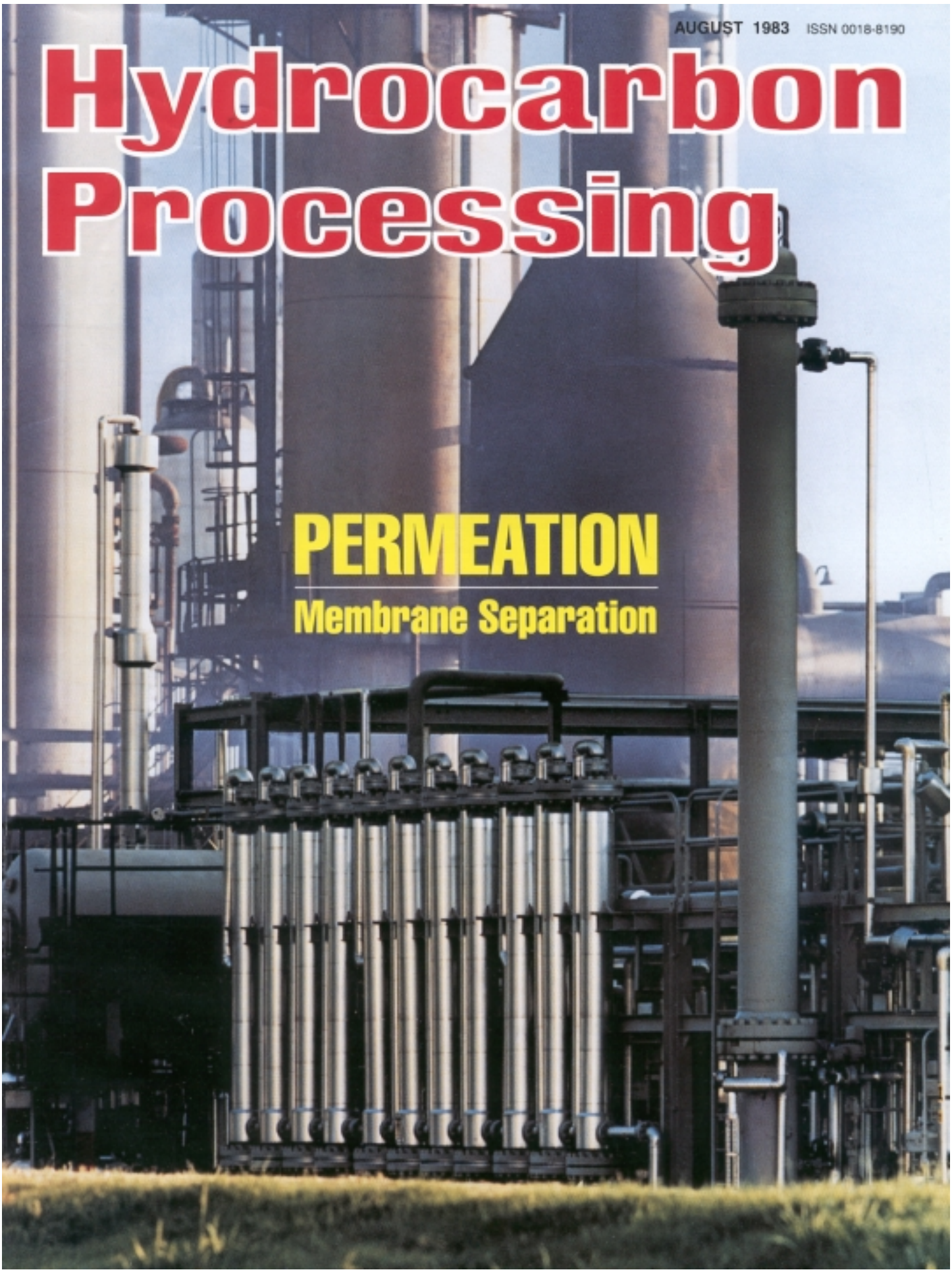
Hydrocarbon Processing



PERMEATION

Membrane Separation

Permeation

Is permeation competitive?

Engineering cost estimates and analyses show that membranes look good in some uses

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THREE MARKETS have the greatest potential for membrane technology when compared with established processes:

- Recovery of hydrogen from ammonia purge streams
- Recovery of hydrogen from hydrotreater off-gas
- Separation of carbon dioxide from hydrocarbons for enhanced oil recovery (EOR).

As membrane technology for gas processing becomes wider spread and more accepted, there will undoubtedly be more applications. There will always be special applications in which membrane technology will uniquely fit.

Membrane systems are simple, straightforward and, therefore, easy to operate and maintain. They require less space than competing processes. Commercial applications of gas separation membranes so far (primarily in hydrogen recovery) have been successful, and membrane life has exceeded expectations. Membrane costs justifiably include recuperation of development expenses now. Thus, there is good reason to expect that the cost will come down significantly in future years as sales volume and competition increases.

On the other hand, membranes are still relatively new. As with any unit, an upset condition not properly designed for can harm a portion of the expensive membrane surface prematurely.

USE IN AMMONIA PLANTS

Ammonia is usually produced by reacting hydrogen and nitrogen at high temperature and pressure over iron catalyst. Natural gas and steam supply the hydrogen while air provides nitrogen. Some methane (natural gas) is not converted to hydrogen and acts as an inert diluent along with argon from the air. Although they do not hurt ammonia synthesis catalysts they depress the hydrogen and nitrogen partial pressure. When energy was cheap, part of the gas circulating in the synthesis loop was purged to the plant fuel system to hold inerts at acceptable levels. Today, energy costs give impetus to recovery of hydrogen and nitrogen from purge gas by recycle to the process in order to save feedstock. First, hydrogen was recovered by ified to take advantage of the capabilities of a purge gas recovery unit (methane content allowed to increase to about double allowed at the entrance to the synthesis loop without purge gas recovery). Pertinent process variables are summarized in Table 1.

The units use very different processes for separation but share similarities. They both must remove ammonia in incoming purge gas to very low levels. Ammonia in high concentration densifies membranes and hampers unit operation while it forms an insoluble solid phase at cryogenic temperatures. In both units, ammonia removal is accomplished with a water scrub. A further purification step is required in the cryogenic unit to remove small amounts of water introduced in scrubbing since it forms a solid phase at cryogenic temperatures. This is normally done with molecular sieves.

Purge gas feed rates through the separation unit are set to hold inerts level in the synthesis loop at a fixed volume. Difference in these rates results from differences in recycle hydrogen stream purities. A slightly purer hydrogen stream in cryogenic operations reduces the amount of returning inerts and reduces feed gas (purge) quantity necessary to hold inerts at a fixed level.

Recompression requirements are greater for returning product from the membrane unit than for the cryogenic unit since membrane separation relies on pressure drop as the driving force while cryogenic

TABLE I-Comparison of membrane and cryogenic-type separation units-process variables

	Membrane Type Monsanto PRISM	Cryogenic Type Petrocarbon -S-2000
Feed Composition, mole%		
H2	60.8	60.8
N2	20.0	20.0
CH4	12.1	12.2
Ar	3.2	3.1
NH3	3.9	3.9
Feed Gas Quantity, lb moles/hr	1,767	1,503
Pressure at Separator Inlet, psig	1,973	1,000
Hydrogen Recovery %	95.7	94.6
Hydrogen Purity, mole%	87.8	92.5
Ammonia Recovery %	99.8	98.7
Recycle Product to High Stage Compressor, %	49.8	100
Recycle Product to Low Stage Compressor, %	50.2	-

TABLE II-Comparison of utilities requirements between membrane and cryogenic type separation units

	Membrane Type Monsanto PRISM	Cryogenic Type Petrocarbon
Electricity, kWh/h	30	80
Cooling water, gpm	200	225
Steam (600 psig), lbs/hr	1,910	1,760
Nitrogen, scfh	Startup only	180
Instrument air, scfh	2,100	1,800
Turbine condensate, gpm	12*	Minor makeup
External power differential kWh/h	470	

* **This process can be modified to use stripper bottoms as the feed ammonia absorbent with only minor effect on cost or utilities consumption.**

separation depends on refrigeration provided by expansion of feed gas and product waste gas. This disadvantage is significant but partially offset because the membrane unit is able to operate closer to purge gas source pressure while the cryogenic unit operates at reduced pressure.

Utilities requirements (Table 11) identify the difference in external power requirements for compressor horsepower based on integrating the purge gas recovery unit into the total plant. The advantage enjoyed by the cryogenic unit is based mainly on hydrogen recycle compression requirement.

Differences in utilities requirements are due largely to the slightly higher feed rate for the membrane unit. Increased power (not including recycle compression) for the cryogenic unit reflects use of electric power to regenerate the mole sieve purification towers. The cryogenic unit also uses a continuous nitrogen sweep of the cold box to guard against explosive mixtures.

Comparative cost and equipment provisions (Table 111) show virtually identical F.O.B. costs although fewer skids and somewhat simpler equipment might give the membrane unit a slight advantage on an installed cost basis. Both units now utilize skid-mounted equipment designs to minimize installation costs.

TABLE III-Comparison of major equipment and F.O.B. equipment costs between membrane and cryogenic type separation units

	Membrane Type Monsanto PRISM	Cryogenic Type Petrocarbon
Equipment costs-F.O.B. at point of manufacture	1,380,000	1,350,000
Number of skids	2	4
Major equipment description	Ammonia stripper skid Prism separator skid	Pretreatment skid Ammonia recovery skid Condensing skid Cold Box plus interconnecting pipework skid

Although both types are highly reliable, membrane units have some operating advantages over cryogenic units.

- They operate at near ambient temperatures, avoiding a cool-down period prior to start-up.
- They have no moving parts other than the scrubber feed pump, while the cryogenic unit requires a mole sieve bed switching system with attendant valves and heater in addition to the scrubber pump.

The extra complexity of the cryogenic unit may result in increased operating and maintenance costs. This will reduce the advantage enjoyed by the cryogenic unit because of lower power requirements.

Hydrogen recovery by membrane separation and cryogenic techniques are competitive. Because of their cost competitiveness and simplicity, membrane separation units are expected to continue to capture a significant portion of the ammonia plant purge gas purification system market.

USE IN HYDROTREATERS

Increasing hydrogen demand in refineries is being met by using a hydrogen recovery unit to reclaim hydrogen from hydrotreater purge gas that normally was burned. Two types of commercially available hydrogen recovery technologies are membrane separation and pressure swing adsorption (PSA).[3]

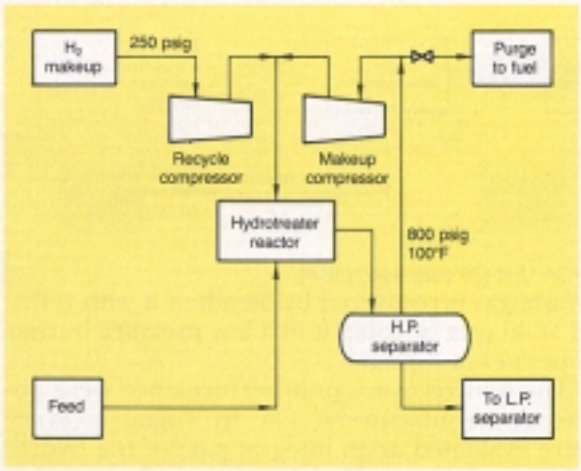

Fig. 1—Existing hydrotreater.

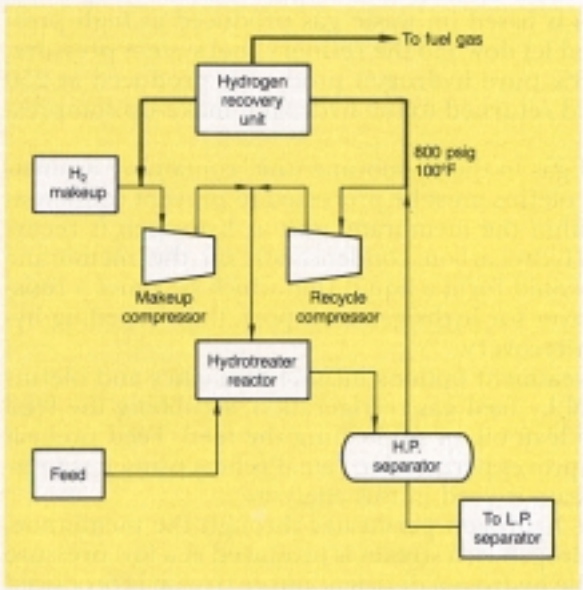

Fig. 2—Integration of a hydrogen recovery unit into a typical hydrotreater.

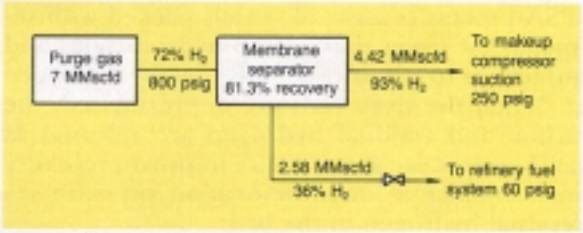

Fig. 3—Membrane separator.

In evaluating the hydrogen recovery units, a typical hydrotreater design is used whose operating conditions are shown in Fig. 1. A slipstream is purged from the high pressure separator to keep inerts at a low level and maintain an adequate hydrogen partial pressure in the reactor. The purge gas is sent to the fuel system.

Hydrogen losses from purge gas can be minimized by use of a hydrogen recovery unit which receives purge gas, recovers hydrogen and feeds it to the hydrogen makeup compressor. Waste gas is sent to the fuel system (Fig. 2).

A 7 MMscfd (end-of-run condition) purge stream is assumed available at 800 psig and 100'F. Product hydrogen is returned to the make-up compressor suction (250 psig) or to the compressor interstage suction (450

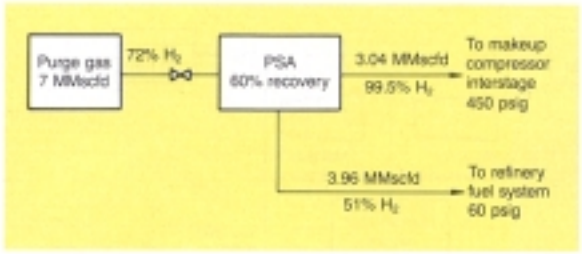

Fig. 4—PSA Unit (70 psig desorption).

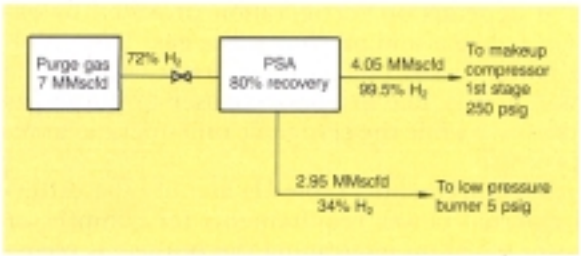

Fig. 5—PSA Unit (5 psig desorption).

psig). Waste gas is recovered by blending it with refinery fuel at 60 psig or using it in a low pressure burner which operates at 5 psig.

Cost data and recovery unit performance were obtained from manufacturers. The hydrogen recovery units were evaluated as an integral part of the hydrotreater heat and material balance.

The material balance of the membrane separator (Fig. 3) is based on waste gas produced at high pressure and let down to the refinery fuel system pressure. The 93% pure hydrogen product is produced at 250 psig and returned to the hydrogen make-up compressor.

Feed gas to the membrane unit, containing aromatics and olefins must be processed to prevent condensation within the membrane unit as hydrogen is recovered. Hydrocarbon condensation on the membrane fibers would form a liquid film which becomes a resistance layer for hydrogen transport, thus impeding hydrogen recovery.

Pretreatment options include aromatics and olefins removal by feed gas refrigeration, scrubbing the feed using a lean oil, or preheating the feed. Feed preheat also improves permeation rate. Preheat using low pressure steam is used in this analysis.

Since hydrogen permeates through the membrane, the hydrogen rich stream is produced at a low pressure while the hydrogen deficient purge stream is produced at a pressure only nominally lower than the feed pressure. Purge gas is throttled down to fuel gas pressure.

The PSA process consists of vessels packed with selective molecular sieves that adsorb hydrocarbons and other impurities to produce a 99%+ purity hydrogen product. When the sieve beds are depressurized, the hydrocarbon and residual hydrogen are released as waste gas. Lower waste gas pressure improves recovery performance, since a lower desorption pressure reduces residual hydrogen in the bed.

Two PSA design alternatives are studied. One operates at 450 psig with a desorption pressure of 70 psig to feed the 60 psig refinery fuel system. The second case operates at 250 psig with a low pressure desorption feeding waste gas to a low pressure burner at 5 psig. (Figs. 4 & 5.)

PSA produces a high purity hydrogen which results in a slightly higher hydrogen partial pressure at the hydrotreater reactor. This means a longer run life for the reactor catalyst or a lower total pressure requirementat the reactor. In this analysis, the lower compression required for the lower total pressure is credited.

PSA bed operating pressures were selected by the manufacturer. The hydrogen product leaving the beds is returned to the makeup compressor. In the high pressure case, hydrogen product from the PSA unit is returned to the compressor interstage suction. The waste gas (desorption) operates at 70 psig. In the low pressure design, hydrogen product is returned to the compressor first stage suction.

TABLE IV-Cost Comparison of Membrane Separator vs PSA

		Membrane	PSA	PSA
Waste gas pressure, psig		-	60	5
H2 Recovery, MMscfd		4.10	3.02	4.05
Capital cost, $M				
	Equipment	530	1,050	875
	Suggested installation by manufacturer	100	175	150
	Total cost	630	1,225	1,025
	H2 Cost, $/Mscf	0.09	0.24	0.15
	Operating cost, $M/yr			
	Steam for feed preheat	10	-	
	Compression to reactor press.	140	46	130
	Contribution to H2 Cost $/Mscf	0.11	0.05	0.09
Total H2 Cost, $/M scf		0.20	0.29	0.24

NOTE: Utility cost based on $.05/kWh and $5/MMBtu.
H2 cost based on 8,000 hours per year operation for a five year span.
For the membrane case, fuel gas is produced at operating pressure and let down to fuel system pressure.

Both membrane separator and PSA units come as shop-assembled systems that are readily skid-mounted. The membrane separator is generally more compact and requires less plot space than PSA.

Equipment and installation costs (Table IV) are for a typical Gulf Coast installation.

Capital cost of membrane separators is lower than for PSA. Total cost of hydrogen is based on a five-year payout. The operating cost of compression of the hydrogen product to the reactor pressure is higher for the membrane case than either PSA case. The compression cost is based on $.05/kWh electric power cost.

Study results show that the total cost for hydrogen recovery is lower in the membrane separator case than the PSA case. Increases in power cost reduce the benefit shown by the membrane case, as would a longer payout period.

Both membrane separator and PSA are readily integrated into the process scheme in retrofitting a hydrotreater with a hydrogen recovery unit. If waste gas must be returned to refinery fuel, the membrane separator is much lower in total cost than PSA. If a low pressure burner is available to utilize the low pressure waste gas from PSA, the cost advantage is reduced.

USE IN EOR

C02 is being used to stimulate oil production in enhanced oil recovery (EOR). Gases associated with EOR vary greatly in composition and volume over the life of the project. Because of the changing nature of the associated gas, membranes should have application in a grass-roots facility as well as upstream of existing gas processing plants. Actual distillation processes used in the field have been described .[4,5] The base case from one operation' for feed gas has been used (Table V

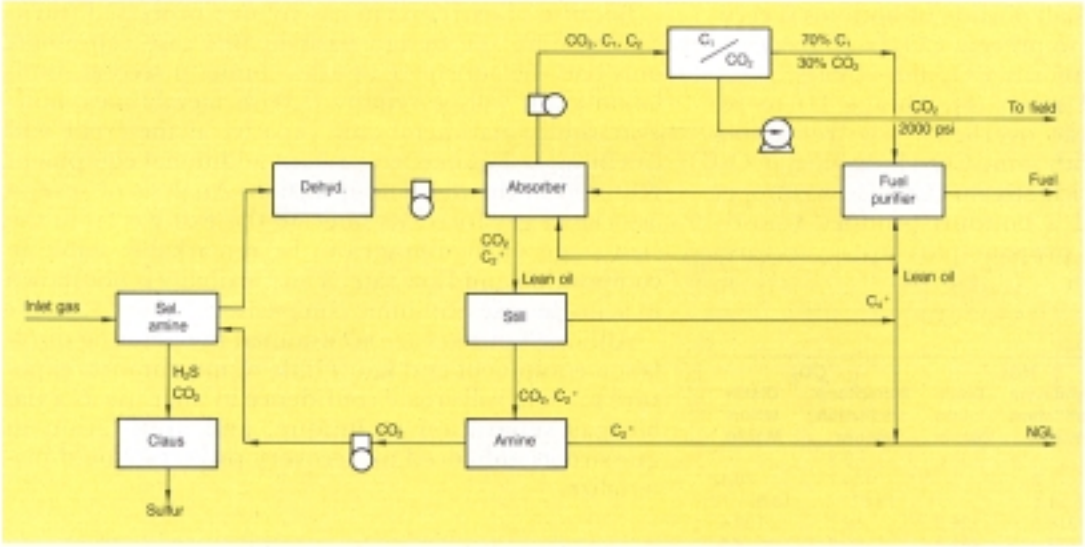

Fig. 6—Distillation block flow diagram.

and Fig. 6) to design a process to duplicate the one described and one using membranes[6] plus distillation (Fig. 7).

Process Description-Distillation Case. Inlet gas is selectively treated to remove H_2S and produce a hydrogen sulfide rich feed gas for feed to a Claus plant for conversion to sulfur. H_2S free gas is dried in a glycol unit, compressed and sent to an absorption column (Absorber) where a C_4^+ lean oil is used to absorb C_2^+ hydrocarbons in the feed. 50% of the C_2 is recovered and 50% escapes with the overhead. A rectifier section

TABLE V-Wasson C02 Plant Design Inlet Gas Composition

Component	Mol%
H2S	**0.05**
C02	**90.25**
N2	**0.16**
C1	**4.76**
C2	**1.75**
C3	**1.52**
iC4	**0.22**
nC4	**0.58**
iC5	**0.21**
nC5	**0.22**
C6'	**0.16**
C7+	**0.12**
	100.00
140 MMscfd	
Press. 275 psig	
Temp. 100 F.	

prevents loss of lean oil components. The CO_2, C_1, C_2 overhead goes to a fractionator (C_1/CO_2) where liquid CO_2 containing ethane is produced as bottoms product and pumped to 2,000 psia for well injection. The overhead is primarily methane but still contains approximately 30% CO_2. A fractionation is again carried out (Fuel Purifier) using lean oil to prevent CO_2 from freezing (Ryan-Holmes process). Fuel gas is produced overhead (2% CO_2) and the bottoms product which contains CO_2^+ lean oil is recycled to the absorber column.

Bottoms from the absorber containing C_2^+ hydrocarbons plus a small amount of CO_2 is fractionated again (Still) to recover lean oil (iC_4^+) Which is recycled back to the absorber and fuel purifier. Overhead is sent to an amine unit to remove CO_2 from the product NGL.

Process Description-Membrane Distillation. H_2S is first removed by selective treating. H_2S free gas is then dried and chilled to remove some heavy hydrocarbon so that condensation does not occur as CO_2 is removed (Hydrocarbon Dew Point Control). Membranes (Membrane I) are next used to remove approximately 90% of the CO_2.

The CO_2 deficient stream, rich in hydrocarbons, is compressed and distilled (Fuel Purifier) to produce methane fuel gas. Bottoms containing C_2 and higher hydrocarbons are distilled again (CO_2 Stripper) to reject

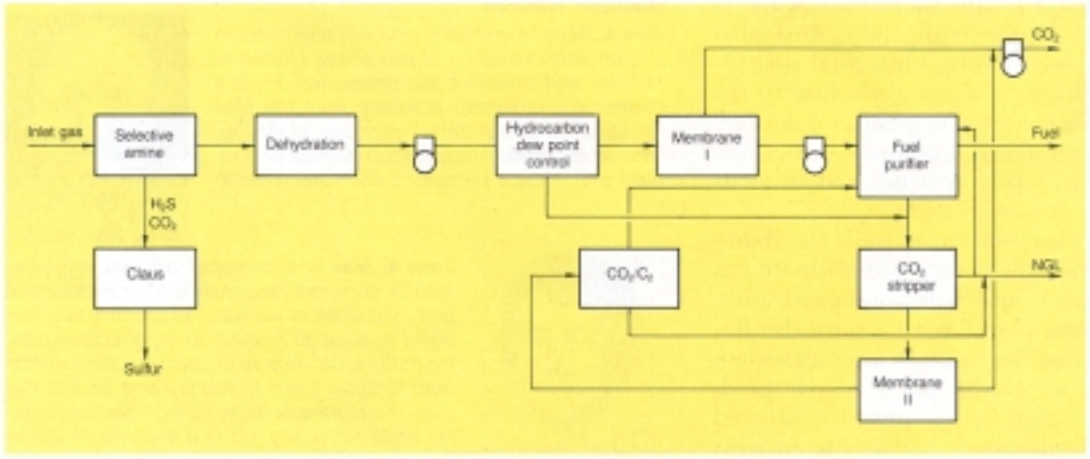

Fig. 7—Membrane separation block flow diagram.

the remaining CO_2. A small portion of bottoms is recycled to the Fuel Purifier to prevent CO_2 from freezing. The overhead contains Mostly CO_2 and ethane.

Membranes are used again (Membrane II) to remove bulk CO_2 from the overhead. The remaining stream (mostly ethane with some CO_2) is distilled (CO_2/ C_2) to produce a CO_2 rich stream (CO_2/C_2 azeotrope) (which is recycled) and a bottoms product, (mostly ethane) which joins the propane-plus stream to form the NGL product stream.

TABLE VI-Products

	FUEL		NGL		C02	
	Membrane distillation	Distil-lation	Membrane distillation	Distil-lation	Membrane distillation	Distil lation
	Mol/hr	Mol/hr	Mol/hr	Mol/hr	Mol/hr	Mol/hr
NO	20.7	24.6			3.9	
C1	597.6	662.5	.2		134.7	70.13
C02	12.7	13.5	1.1		13,871.4	13,871.73
C2	1.8	0.4	214.0	136.6	52.7	132.4
C3+	1.1		436.4	461.7	30.2	4.5
TOTAL	633.9	701.1	651.7	586.8	14,092.9	14,078.8
mm Btu/hr (HHV)	230.5	253.3	669.5	644.5	-	-

Comparison. In the distillation case, most hydrocarbon loss is ethane, which escapes with the CO_2. This loss contains approximately 50% of the ethane in the feed. In the combination process, some of each component escapes with the CO_2. Thus, for the membrane case the methane fuel gas is 9% less than in the distillation case (Btu basis), and the NGL stream is 4% greater (Btu basis). (Table VI). The NGL stream from the combination process has more ethane and less C_3^+. Net recovered hydrocarbon on a Btu basis for both fuel gas and NGL streams is essentially identical in the two cases.

TABLE VII-Variation in operating costs for membrane-distillation process relative to distillation process

Power	+$0.8MM/yr	
Heat	-$2.8MM/yr	
Membrane	+$1.2MM/yr	
Net	- $0.8MM/yr	(-$.02/Mscf CO2)

Approximately 3,000 additional

Approximately 3,000 additional horsepower are required in the combination case, but 100 MMBtu/h less heat is required resulting in a net advantage for the membrane combination process that is offset by membrane replacement cost6 (Table ASCII). With an assumed membrane life of three years, $3.50/MM Btu and $0.05/ kWh, net operating cost for the membrane case is lower, but only by 5%. Major equipment cost also turned out nearly identical, although installed cost favor the membrane distillation case slightly due to reduced installation cost for the smaller plant. Of course, the major cost item in both plants is compression, since feed gas (90% CO2 at 275 psig is processed to yield C02 at 2,000 psi.

The real advantage with membrane use is flexibility and modular design. A reliable forecast of ultimate gas production is not required, and will not significantly affect the economics of the, plant. With a pure distillation scheme, a plant must be built to accommodate forecasted gas production. If the plant is oversized, this will result in extra capital being spent for unused capacity; if the plant is undersized, inability to process gas may limit oil production.

Because of extremes in gas volume processed (turndown ratio), the design basis in this case represents only half the anticipated peak volume. A second distillation plant will be required. With membranes, however, additional membrane capacity at the front end can be added as needed without additional equipment required in the distillation section. Analysis of several associated gas forecasts indicate the exit gas from the first stage of membranes to be remarkably stable in composition and flow rate. This flexibility is not shown in a single case economic comparison.

Although owners are accustomed to operating distillation equipment and know little of membranes, exposure to them will create confidence in their use as a viable gas separation technique, and application to grass-roots enhanced oil recovery projects should materialize.

Conclusion. We have attempted to examine three areas where gas separation membranes are competitive with conventional technology. In each case, membranes were shown to be at least on a par with alternate conventional technology, and in each case, characteristics of the membrane system and the alternate would play an important role in the ultimate decision of which process is chosen. Membranes have a definite place in gas processing and will find greater application in the years to come.

ACKNOWLEDGMENTS

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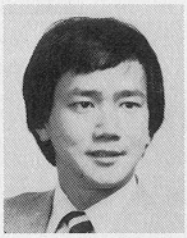

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