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ADVANCED MEMBRANE DEVICES

Interim Report for the Period
October 1996 - September 1997

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PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract DE-FC36-94GO10004

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1.0 Executive Summary

Under this Cooperative Agreement, Air Products and Chemicals, Inc. has continued to investigate and develop improved membrane technology for removal of carbon dioxide from natural gas. The task schedule for this reporting period included a detailed assessment of the market opportunity (Chapter 2), continued development and evaluation of membranes and membrane polymers (Chapter 3) and a detailed economic analysis comparing the potential of Air Products membranes to that of established acid gas removal processes (Chapter 4). These sections are summarized below, along with recommendations for further work.

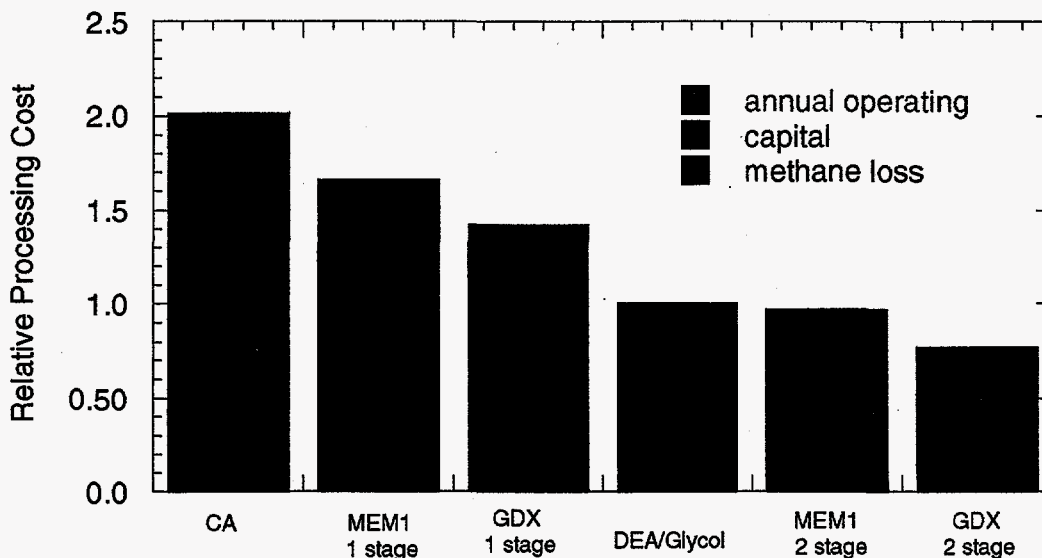
Natural gas processing encompasses six separations, valued at more than \$7 billion/yr in the U.S. alone. Natural gas will continue to be the fastest growing worldwide energy source through 2015, while U.S. gas consumption is projected to grow 2-3%/year through 2015. Production in the Gulf of Mexico, Colorado, and Wyoming is expected to increase faster than the U.S. average, and may require grass-roots facilities. There is also a potential for incremental expansion in many regions, since the most productive fields are being extended through deeper drilling.

About 25-30% excess gas processing capacity exists in the U.S., although it is not evenly distributed. Stagnant or declining production in several major hydrocarbon regions will probably feed the already active used-equipment market. However, there will likely be opportunities for new equipment because there has been little grass-roots construction in the U.S. in the past several years, and the requirements for some separations, such as small, remote CO₂ removal, cannot be addressed by the existing infrastructure.

In laboratory work, it was demonstrated that GDX, a new membrane polymer, could be spun into hollow-fiber membranes. Laboratory modules were evaluated for pure gas CO₂ and CH₄ permeability. The results demonstrate that the fiber spun during pilot plant trials was defect repairable to intrinsic selectivity. At 23°C, the CO₂ permeance showed a marked increase at CO₂ pressures above 300 psig, indicating that CO₂ was plasticizing the polymer. This effect was not observed at 50°C, where CO₂ activity is lower. Additional evidence was found in the CO₂ adsorption isotherms for this polymer. GDX results were compared to a benchmark polymer MEM1, which displayed a lower degree of plasticization at 23°C. Preliminary mixed-gas testing indicated no mixed-gas effects for either GDX or MEM1.

An in-depth economic evaluation of the different CO₂ removal techniques from natural gas was performed. The purpose of this evaluation was to compare current technology economics to those for a new membrane polymer currently being explored under this Cooperative Agreement. Intrinsic permeation data was obtained on this new polymer as well as on benchmark membranes (MEM1 and MEM2). The data was used as input to an Aspen computer model to calculate the area requirements for both single and two-stage configurations as applied to our study case. The estimated membrane area was then used as inputs to a membrane-costing evaluation program to determine the overall gas processing costs (measured in \$/MSCF feed) associated with the technology. Economic and process performance data accumulated for other competing membrane technologies, as well as the primary non-membrane technology (amine scrubbers for CO₂ removal and glycol systems for dehydration), were also evaluated using the same base case conditions. The conclusions from this study were that GDX provided the lowest processing cost alternative among the *single-stage* membrane systems presented, but the predominant technology of amine scrubbers (CO₂ removal) and glycol dehydrators still showed a 30% lower customer cost than the GDX membrane. This cost savings is primarily due to higher methane losses in the membrane systems. To lower these methane losses, a two-stage configuration of the same polymer was evaluated. A conventional two-stage design with permeate recompression was used with both MEM1 and GDX membrane modules to determine the processing costs. It was determined that both the MEM1 and GDX two-stage systems displayed more favorable economics than both single-stage designs or a scrubber/dehydrator. The two-stage GDX system provided the lowest overall processing costs. These results are summarized in Figure 1-1. Sensitivities to flow rate and feed CO₂ content help determine what operating conditions enhance the advantages of the two-stage design. Additionally, intangible membrane technology benefits not associated with economics (e.g., lack of moving parts, smaller space/weight requirements) must be considered in assessing competitive technology.

Figure 1-1 - Summary of Comparative Acid Gas Removal Technologies



Key: CA = cellulose acetate spiral-wound membrane
GDX = Air Products advanced polymer membrane
MEM1 = benchmark membrane
DEA/Glycol = diethanolamine/glycol conventional acid gas scrubbing/dehydration system

Recommendations for Further Work

As a result of work performed during this reporting period, Air Products recommends the following tasks to complete this program and demonstrate viable advanced membrane technology. Each task is described in detail in the Statement of Work for this Cooperative Agreement.

- Initiate laboratory challenge testing on small modules to examine the effects of wellhead gas contaminants on membrane performance (e.g., water vapor, low-level hydrocarbons, low-level hydrogen sulfide).
- Initiate field testing of MEM1, GDX and subsequent new polymers achieving preliminary targets as set forth in this report. To ensure maximum utility of the field test data, testing will be conducted on the largest size modules that can be reasonably fabricated under this agreement. The goal is to evaluate full-size commercial units and confirm laboratory properties.
- Continue development of next-generation polymer membrane materials as per the Statement of Work for this Cooperative Agreement.

Successful performance of these tasks will lead to a decision on a commercially viable membrane system and result in the completion of this program.

2.0 Market Assessment

Summary

Natural gas processing encompasses six separations, valued at more than \$7 billion/yr in the U.S. alone. Natural gas is the fastest growing worldwide energy source through 2015, while U.S. gas consumption is projected to grow 2-3%/year through 2015. Production in the Gulf of Mexico, Colorado, and Wyoming is expected to grow faster than the U.S. average, and may require grass-roots facilities. There is also a potential for incremental expansion in many regions, since the most productive fields are being extended through deeper drilling.

About 25-30% excess gas processing capacity exists in the U.S., although it is not evenly distributed. Stagnant or declining production in several major hydrocarbon regions will probably feed the already active used equipment market. However, there will likely be opportunities for new equipment because there has been little grass-roots construction in the U.S. in the past several years, and the requirements for some separations, such as small, remote CO₂ removal, cannot be addressed by the existing infrastructure.

2.1 Natural Gas Processing Overview

Natural gas processing represents one of the largest markets for gas separation equipment, with operating costs in the U.S. exceeding \$7 billion/yr. The required processes and specific types of equipment are determined by pipeline requirements and wellhead composition. Gas composition varies widely with respect to methane, natural gas liquids (C₂+), H₂O, CO₂, H₂S, N₂, and He. Consequently, six generic separation applications are practiced by the industry to remove undesirable species and/or recover higher value products. They are listed in order of size below:

- Natural gas dehydration
- Natural gas liquids recovery
- Acid gas removal
- Sulfur recovery
- Nitrogen rejection
- Helium recovery

Only acid gas removal (AGR) will be addressed in detail in this report. As shown in Table 2-1, AGR processes comprise over 600 installations and represent almost a billion dollars a year.

Table 2-1 - Acid Gas Separations

Generic Separation	Number of Lower-48 U.S. Plants	Extent of Use ¹	Annual Processing Cost
Acid Gas (CO ₂ and H ₂ S) Removal	617	8% high for CO ₂ only 5% high for H ₂ S only 9% high for CO ₂ and H ₂ S	\$0.8 B

2.1.1 Industry Overview

Natural gas processing is an intermediate step in a sequence that begins with gas exploration and ends at the consumer's point-of-use. The cost of this sequence of processes exceeds \$7 billion/yr. The cost of processing relative to other operational inputs is illustrated by the Sterling Consulting Group's study for the Gas Research Institute (GRI)². They segmented the U.S. natural gas industry into producers, processors, and pipelines to provide an overview of the value added by key activities of the industry, from the well to the interstate pipeline. A summary of the incremental values is shown in Table 2-2.

Table 2-2 - Value-Added Chain for the Natural Gas Industry (2)

Activity	Cumulative Cost (\$/MSCF)
Gas Acquisition (exploration or purchase)	\$0.63
Gas Production	\$1.66
Gathering and Processing	\$1.77
Interstate Pipeline to Citygate ³	\$2.78
Residential Consumer ³	\$6.06

The first steps in the value chain are activities by producers. Acquisition of reserves in the ground establishes an average U.S. market price of \$0.63/MSCF. Producers extract the gas from the ground and dehydrate it, increasing its wellhead value to \$1.66/MSCF. All gas requires dehydration, typically via absorption into triethylene glycol at a cost of \$0.04-0.08/MSCF⁴. In the U.S., 74% of the gas produced in 1991 required only natural gas dehydration (NGD) to meet pipeline specifications.⁵ Producers are the customers for dehydration equipment, and there are over 7000 producers in the U.S. Hence, the NGD equipment market has the largest gas processing volume and the most diverse customer base.

Producers generally do not further treat their gas. Natural gas liquids (NGL) recovery, acid gas separations, nitrogen rejection, and helium recovery are generally performed by the gathering and processing industry, which usually is an entity unrelated to the producer. These markets are smaller than the NGD market, and have a different customer base. The exceptions are remote gas wells and offshore wells, where NGL recovery and/or acid gas removal may be performed by the producer.

The gathering and processing industry is responsible for the network of compressors and pipelines that connects the gas production fields to gas processing plants. It collects the gas, moves it to the interstate pipelines, and performs the required conditioning, treating, and removal of higher valued components. As shown in Table 2-2, it represents the smallest cost increment in the natural gas value chain. The U.S. and Canadian industry is characterized by two types of plants, field plants and straddle plants. NGL recovery drives the industry, which processes approximately 74% of all U.S. gas.

Gas processors receive a fee for removing acid gas and N₂. NGL recovery may be mandatory to meet the hydrocarbon dewpoint limit, or may be optional, depending on the value of the NGL stream relative to recovery costs. If the NGL does not generate sufficient profit for the gatherer/processor, a fee is negotiated whereby the producer pays the gather/processor for gas conditioning. Generally NGL values exceed their recovery cost and their energy value if sold as natural gas. Producers and processors use various contractual arrangements to cover the risk associated with the pricing differential between NGL and natural gas.⁴ NGL values are established by transactions between producers and their consumers, primarily refineries and chemical companies. The value of NGL is adjusted by the cost of its transportation (typically the Gulf Coast) and its fractionation into pure components.

Field plants are fed by a dedicated pipeline network that collects wellhead gas from one or more proximal fields. Field plants typically recover NGL. Some field plants also practice acid gas removal (which requires subsequent downstream dehydration). If the sulfur content of the gas is sufficiently high, the field plant may include sulfur recovery to reduce SO₂ emissions. Approximately 18% of the gas in the U.S. requires acid gas treatment, at a cost of \$0.1-0.2/MSCF⁴. The other separations, N₂ rejection and He recovery, are relatively rare and are always associated with NGL recovery. After processing, the conditioned natural gas (called residue gas if NGL recovery is practiced) is fed to interstate pipelines for distribution. The average size for a field plant is less than 25 MMSCFD.

Straddle plants recover NGL from interstate pipelines, and may include fractionation. The largest straddle plants require sulfur recovery units to reduce SO₂ emissions. Because straddle plants receive gas directly from transportation pipelines, the feed has a low NGL content. These plants rely on large scale to be economical, and generally are significantly larger than field plants. The U.S. has about 35 straddle plants larger than 500 MMSCFD.

The gathering and processing industry is the customer for all the various types of gas processing equipment. A recent GRI study concluded that this industry is fragmented, with over 150 participants.⁶ The dominant players have less than 10% market share based on volume of gas processed. The U.S. industry has a capacity of 69 BSCFD (exclusive of dehydration), which operated at 70% capacity in 1995, up from an average capacity utilization of 62% for the previous five years.

2.2 Processing Requirements

The difference between gas wellhead composition and interstate pipeline requirements determines which gas separations need to be practiced. Government regulations also have an impact on technology choices. These factors are briefly reviewed.

2.2.1 North American Requirements

Natural gas must meet pipeline quality specifications to reach the market. Gas must be free of liquids (hydrocarbons and water) to be measured accurately and prevent slugs from plugging the pipelines or damaging compressors. Water content is reduced to prevent freezing or formation of hydrates, which are solid water/hydrocarbon compounds. Pipelines limit CO₂ due to its corrosive properties. H₂S is also corrosive, but is removed primarily because it is toxic at low concentrations. Natural gas may also contain nitrogen in significant quantities. Although harmless, it adds to compression cost and reduces the calorific value of the gas.

Pipeline specifications for the U.S. are summarized in Table 2-3.

Table 2-3 - Interstate Gas Pipeline Specifications (4)

Water Vapor	7 lb/MMSCF, typical for lower 48 States 4 lb/MMSCF for pipelines close to the Canadian border, North Sea, and deepwater GOM
Carbon Dioxide	1-3%, typically 2%
Hydrogen Sulfide	Typically ¼ grain per 100 SCF (4 ppm)
Nitrogen	Normally addressed in combination with other inerts. Typical is 4% inerts (CO ₂ and N ₂) by volume. Alternately pipelines specify a lower heating value limit, which averages 970 BTU/SCF.
Liquid Hydrocarbons	Specifications vary. Typical hydrocarbon dewpoint is 10-15°F @ 800 psi. Alternate specifications on C5+ (gasoline) content, or maximum BTU content
Solids, Dust and Gum	Free
Oxygen	0.2%
Mercaptans	5 grains/100 SCF
Total Sulfur	12 grains/100 SCF
Heating Value	>950 BTU/SCF
Temperature	40 to 120°F

2.2.2 Regulatory Requirements

Government regulations also impact the technology choices in gas processing. The major constraints include:

- Benzene, ethyl benzene, toluene, and xylene (BTEX) and other VOCs emitted from the reboiler still vent of glycol dehydrators. For many dehydrators, emissions of BTEX and other HAPs are likely to exceed the major source HAP emissions thresholds cited in Section 112 (a) of the 1990 Clean Air Act Amendments. The Emission Standards Division of OAQPS has in development proposed Maximum Achievable Control Technology (MACT) emissions standards for glycol dehydrators.⁷ GRI and others have developed back-end treatment to reduce emissions from glycol units.
- Natural gas flaring is generally prohibited in both the U.S. and Canada, forcing oil wells to separate and re-inject gas where marketing the gas is not possible.
- Methane emissions are restricted in some European countries, and may be restricted in the U.S. and Canada in the future due to global warming initiatives.

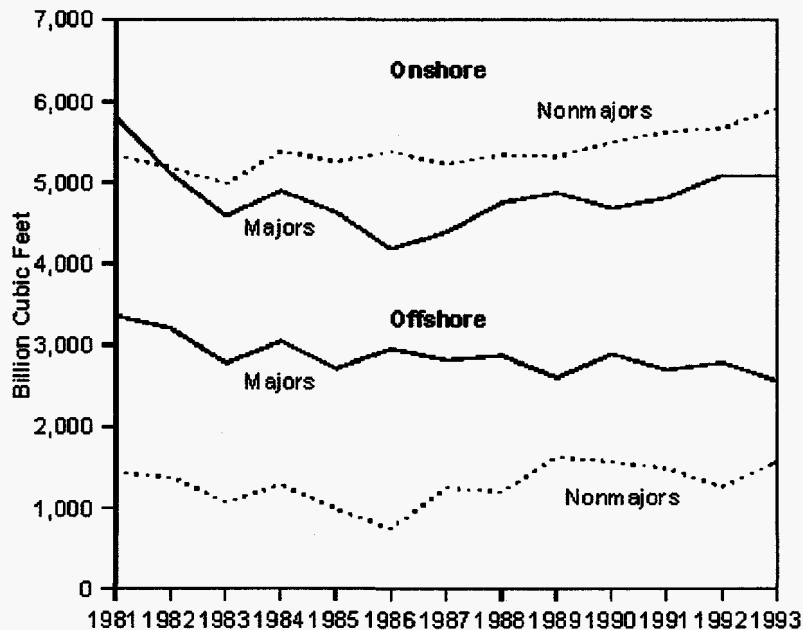
2.3 Customers for Natural Gas Processing Equipment

There are three sets of customers for gas processing equipment: producers, processors, and engineering firms. Introducing new processing equipment will require addressing all three customer bases.

Producers purchase most natural gas dehydration (NGD) equipment, since it is typically deployed at the wellhead. Producers also purchase acid gas and NGL removal equipment, when required, for offshore platforms because process equipment must be integrated into the production platform design. For remote gas wells not serviced by field plants, producers will sometimes purchase acid gas and NGL removal equipment as well. The regions with the fastest growth for acid gas removal equipment tend to be remote. These two trends suggest that producers will be important customers for polymer membrane NGD and acid gas removal systems.

Producers are traditionally characterized as majors and non-majors, with the non-majors further divided into independents and small private producers. Onshore and offshore gas production for majors and non-majors is shown in Figure 2-1.⁸ The profile of producing companies has changed dramatically since the oil price collapse of late 1985 and early 1986.⁹ In 1992, there were 327 publicly traded corporations whose primary industry was oil and gas extraction, and about 7400 small private producers. Investment by the non-majors, primarily the independents, increased from about 33% of total U.S. exploration and development expenditures in 1988-1990 to nearly 50% in recent years. The small, private producers accounted for 30% of U.S. oil and gas production in 1993. The large number of producers will make it challenging to identify the customers for NGD systems and remote CO₂ or NGL systems.

Figure 2-1 - U.S. Natural Gas Production for Majors and Nonmajors (8)



The other two types of customers are gas processors and engineering firms. As discussed above, the processing industry comprises more than 150 companies. Gas processors procure the NGL, acid gas, and nitrogen rejection equipment. Where acid gas treatment is required, the gas will generally require downstream dehydration as well. Processors complement their technical departments with varying levels of input from the engineering companies. Shell and Chevron noted that larger, more sophisticated companies traditionally made their own process technology selection. Engineering companies, which license process technology, provide bids for the majors during process evaluation and typically construct gas plants. In the past, the processing companies were the primary customers for new equipment.

Engineering firms may become more important as customers for new equipment due to the decline of the majors and rise of smaller players in gas processing. The trend has been for the majors to restructure or exit the processing business due to excess capacity and recent weak gas processing economics.¹⁰ Most restructuring has resulted in companies with intense natural gas marketing programs, rather than technical focus. For example, Amoco and Shell recently merged their Permian Basin production and processing assets into a new independent company, Altura Energy. For the past three years, the majors have had significant downsizing of technical staff, and no large grassroots gas plants have been built in the U.S. or Canada. Consequently, their ability or desire to screen new process technology may not be as strong as in the past.

2.4 U.S. Gas Processing Equipment Market

The market for gas processing equipment includes replacement of existing infrastructure, as well as construction of new plants to meet projected growth in total gas production. This section first reviews the current makeup of the U.S. gas processing industry for AGR, including the market shares and economics for specific technologies. Next, we discuss the projected changes in the composition of U.S. gas production through 2015.

2.4.1 Current U.S. Gas Processing Infrastructure

The number of plants, market share for specific processes, approximate volume of gas, and revenue are estimated for each of the gas separation applications. The information is based primarily on a Purvin and Gertz report for GRI¹¹ and the database of U.S. NGL plants from EIA. Excluding NGD, the U.S. industry has a capacity of 69 BSCFD, which operated at 70% capacity in 1995, up from an average capacity utilization of 62% for the previous five years. Major gas producers are noted in Table A1 in the Appendix to this chapter.

As noted above, about 74% of U.S. natural gas requires only dehydration to meet pipeline specifications. Absorption with triethylene glycol is used almost exclusively. Although generally not required, over 70% of U.S. gas is treated for NGL recovery due to the favorable price differential between methane and NGL. There are several processes that have niches in terms of size, operating cost, and NGL recovery factor. Eighteen percent of the gas requires acid gas treatment, which typically involves only CO₂ removal. There is a broad spectrum of processes for H₂S removal, with the optimal choice depending on H₂S and CO₂ concentrations as well as gas flow rate. Nitrogen rejection and helium recovery are relatively rare, since they require expensive cryogenic processes.

2.4.2 Acid Gas Processes

Acid gas (CO₂ and H₂S) is predominantly removed by a variety of solvent processes, depending on the concentrations of CO₂ and H₂S. The most common solvent is diethyl amine (DEA), although other alkanol amines are also used. The alkanol amines do not have good selectivity for H₂S over CO₂, and so are typically used where only CO₂ removal is required. About 8% of U.S. gas requires CO₂ removal only. Not of all this gas is treated, however; some is blended into the pipeline. The annual operating cost for the amine plants, which represents most acid gas plant capacity, is \$0.8 billion/yr.

The types of acid gas processes for the U.S. are listed in Table 2-4. Alkanol amines, particularly DEA, have most of the capacity. The average capacity of both the chemical and physical solvents is about 90 MMSCFD. Note that there are relatively few physical solvent systems.

Table 2-4 - Summary of U.S. Acid Gas Plants¹²

Process		Process Total
Chemical Solvent Processes		
	MEA	116
	DEA	189
	MDEA	30
	DGA	36
	Benfield	7
	Other	16
	Total	394
Physical Solvent Processes		
	Sulfinol	57
	Selexol	5
	Other	4
	Total	66

2.4.3 U.S. Production Through 2015

U.S. natural gas gross withdrawals have increased at an average rate of 1.9%/year for the past 10 years to their current level of 23.7 TSCF/yr (trillion standard cubic feet/year)¹³. A summary of production statistics for 1970 through 1995 is provided in the Appendix. GRI's projections for U.S. natural gas consumption are shown in Table 2-5. GRI expects consumption to grow from 21.2 TSCF in 1994 to 28.7 TSCF by 2015, surpassing the 1972 high of 22.5 TSCF before 2000.¹⁴ GRI estimates a 3% growth rate for the next 10 years, significantly higher than the growth rate for the past 10 years. Natural gas share of total primary energy consumption will increase from 24.1% in 1994 to almost 26% by 2015, driven largely by displacement of oil for process heating and power generation. The Energy Institute of America's (EIA's) estimate for North America is 1.9%/year through 2015¹⁵, about equal to the average U.S. growth rate over the past decade. Estimated natural gas consumption is 26.9 trillion cubic feet in the GRI forecast, with the EIA forecast falling near the middle at 24.6 trillion cubic feet.

Table 2-5 - Projected U.S. Natural Gas Consumption in TSCF (14)

Year	1994	2000	2010	2015
Segment				
Residential	5.0	5.2	5.5	5.8
Industrial	9.5	10.1	11.4	11.8
Gross	2.1	2.5	3.1	3.2
Cogeneration ^a				
Net	1.1	1.3	1.5	1.6
Cogeneration ^b				
Electric Generation ^d	3.2	4.5	5.9	6.3
Transportation	0.7	0.8	1.2	1.5
Vehicles	(c)	(c)	0.4	0.6
Pipeline	0.7	0.7	0.8	0.9
Total Gas Consumption	21.2	23.5	27.3	28.7

a) Includes total natural gas consumption in a cogeneration system.

b) Includes only the natural gas consumed in a cogeneration system attributable to the incremental energy required to generate electricity.

c) Less than 0.05 TSCF.

d) Includes central utilities, independent power producers, and exempt wholesale generators.

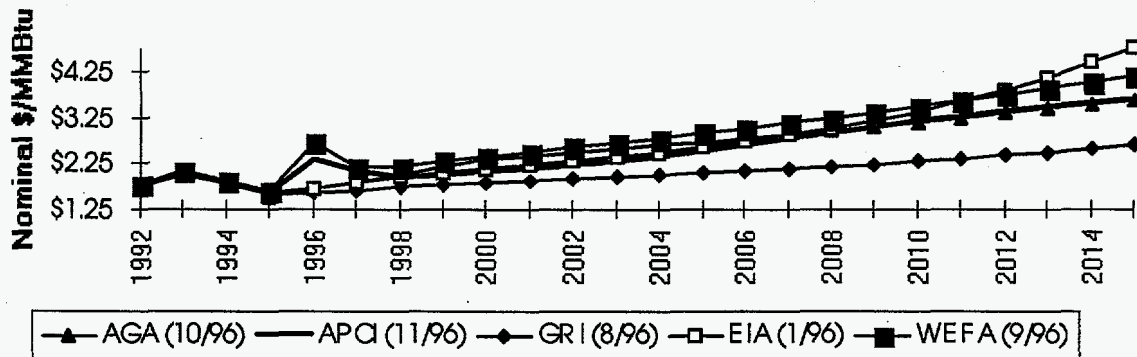
e) Includes 0.2 TSCF of "other" gas, primarily SNG from petroleum and miscellaneous gases, and high-BTU coal gas, in 2000, 2010, and 2015, respectively.

The wide range of natural gas forecasts highlights the uncertainty about future market directions. The greater consumption in the GRI forecast can be attributed, at least in part, to a wellhead price forecast that falls considerably below the others, as shown in Figure 2-2. The GRI wellhead price is driven by a number of supply-related assumptions, including GRI's characterization of the resource base. Due to the uncertainty in projections, estimates for equipment markets are based on projected gas production in 2000. Note that Canadian imports will likely play an increasing role in U.S. gas supply, so not all incremental production will come from the U.S.

Demand for gas processing equipment depends on the composition of the gas, as well as the total volume produced. Information on U.S. gas composition is available through the DOE GASIS project, on which Energy and Environmental Analysis, Inc. is the lead.¹⁶ GASIS will provide a searchable database of all U.S. natural gas formations and wells. The preliminary CD ROM is now available.

Figure 2-2 Natural Gas Costs as Projected by Air Products and Others

COMPARISON OF NATURAL GAS PRICE FORECASTS
(\$/MMBtu)

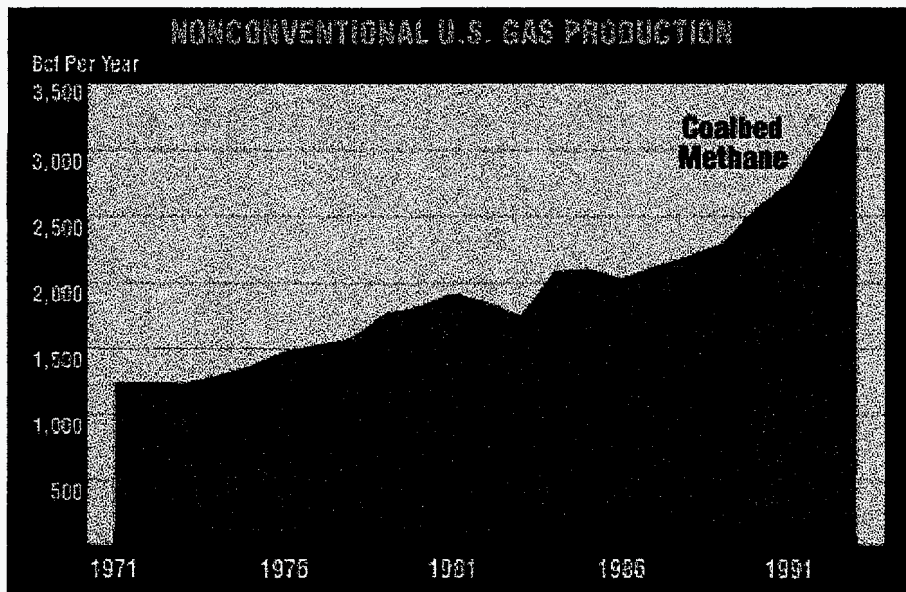


The sources of future U.S. production include the current reserves and new finds. U.S. dry natural gas reserves were 165 TSCF in 1995. Dry gas reserves are the total non-associated gas and associated-dissolved gas reserves adjusted for the removal of liquids at natural gas processing plants. U.S. reserves are concentrated in Texas (22%), the Gulf of Mexico Federal Offshore (17%), New Mexico (11%), Oklahoma (8%), and Wyoming (7%). Reserves are listed by state in Table A3 in the Appendix following this chapter. Given the current average production exceeding 20 TSCF/year, the current reserves would be expected to last about 7 years.

New gas discoveries are the second source of future gas production. The U.S. gas supply has increased almost 30% since 1986, returning to its highest level since 1974. One reason for expansion of gas supplies is the discovery of significant gas in existing onshore Lower-48 fields below 10,000 feet. The large decline in gas production observed between 1973 and 1986 reflected a severe falloff in onshore gas production from older fields as industry activity depleted many established areas and conventional gas reservoirs above 10,000 feet. Exploration and development activity was heavily concentrated above 10,000 feet, although the "quality" of new field discoveries below 10,000 feet was generally much better. By the mid to late 1980s, production from older Lower-48 fields stopped declining and began to increase as deeper wells were completed. The trends in stable recovery in the older fields have been long term, extending over as much as 60% of the total activity in the older fields. The extension of the older fields means the industry will continue to rely on existing gas processing infrastructure, with only incremental equipment additions.

The second source of new gas supplies is non-conventional gas, including tight reservoirs, coal-bed methane, and shale.¹⁷ Figure 2-3 shows the increase in non-conventional gas production from 1971 through 1993. During this time, tight gas production increased from 1,091 to 2,626 BSCF per year, coal bed methane production increased from nearly zero to 732 BSCF per year, and Devonian/Antrim shale gas production increased from 149 to 289 BSCF per year. Total non-conventional production in the U.S. increased from 1,240 to 3,647 BSCF. The fraction of U.S. dry gas production represented by non-conventional gas rose from 5.7% in 1971 to 20.0% in 1993. GRI predicted non-conventional production of 3.9 TSCF in 2000 and 8.4 TSCF in 2015, more than one-third of Lower-48 gas production in 2015. They noted that non-conventional gas production increased in recent years despite low gas prices and the phasing out of tax incentives. The primary reason is advances in production technology. GRI predicts that growth in Lower-48 gas production after the year 2005 will be dominated by increased production from less conventional gas sources, principally low-permeability reservoirs.

Figure 2-3 - Non-Conventional U.S. Gas Production (17)



Energy and Environmental Analysis, Inc. (EEA) provided a breakout of U.S. production for 1991 and projected production for 2000 as a function of hydrocarbon region (i.e., location), N_2 , CO_2 concentration, H_2S concentration, NGL content, and gas type (associated/non-associated). Note that EEA's hydrocarbon model, which incorporates well field activity, reserve additions, gas composition, and overall gas economics, is used by GRI for their annual projection of future gas production. They have predicted U.S. gas production through 2015 for GRI. The EEA database on two important regions, the Gulf of Mexico (GOM) and the Antrim formation in Michigan, is limited. Much of the gas composition for the Gulf of Mexico is not publicly available.

Table 2-6 - Year 2000 U.S. Gas Production by Processing Requirement (Volumes in BSCF)

Category	N ₂	CO ₂	H ₂ S	Lower-48
CO₂ Removal				
5	< 4%	2 TO 7%	< 4 PPM	1,520
9	< 4%	GT 7%	< 4 PPM	488
H₂S and CO₂ Removal				
6A	< 4%	2 TO 7%	4 -10 PPM	48
6B	< 4%	2 TO 7%	11 -35 PPM	66
6C	< 4%	2 TO 7%	36 -100 PPM	56
7A	< 4%	2 TO 7%	101-3,300 PPM	444
7B	< 4%	2 TO 7%	3,301-10,000 PPM	140
8A	< 4%	2 TO 7%	10,001-30,000 PPM	201
8B	< 4%	2 TO 7%	>30,000 PPM	341
10A	< 4%	> 7%	4 -10 PPM	14
10B	< 4%	> 7%	11 -35 PPM	20
10C	< 4%	> 7%	36 -100 PPM	17
11A	< 4%	> 7%	101-3,300 PPM	31
11B	< 4%	> 7%	3,301-10,000 PPM	10
12A	< 4%	> 7%	10,001-30,000 PPM	62
12B	< 4%	> 7%	>30,000 PPM	106
TOTALS				3564

2.4.4. Projected U.S. Gas Processing Equipment Requirements

In 1991, GRI published an assessment of gas processing equipment requirements for 2000.¹⁸ The report grouped facilities into five functions: dehydration, treating for carbon dioxide and hydrogen sulfide removal, natural gas liquids extraction, nitrogen removal, and sulfur recovery. They concluded that there were 694 existing AGR treating facilities in the U.S. and that additional capacity would be required in the near future. In retrospect, the study overestimated equipment demands in each category. GRI's effort suggests the hazards of estimating the process equipment market.

In the current study, the market for gas processing equipment has been estimated by comparing the processing requirements for gas production in 1991 against the processing requirements for EEA's estimated gas production in 2000. Table 2-7 summarizes the estimated changes in gas production by region, and the corresponding types of processing that are required. More detailed analysis for 1991 and 2000 production and reserves as a function of location, composition, and type (associated/non-associated) are available in a series of proprietary spreadsheets. The following sections summarize the significant opportunities for NGD, acid gas processing, and nitrogen recovery.

Table 2-7 - Difference in U.S. Gas Production from 1991 to 2000 (Volumes in BSCF)

Category	N ₂	CO ₂	H ₂ S	Lower-48
CO₂ Removal				
5	< 4%	2 TO 7%	< 4 PPM	365
9	< 4%	GT 7%	< 4 PPM	222
H₂S and CO₂ Removal				
6A	< 4%	2 TO 7%	4-10 PPM	4
6B	< 4%	2 TO 7%	11-35 PPM	6
6C	< 4%	2 TO 7%	36-100 PPM	5
7A	< 4%	2 TO 7%	101-3,300 PPM	233
7B	< 4%	2 TO 7%	3,301-10,000 PPM	73
8A	< 4%	2 TO 7%	10,001-30,000 PPM	154
8B	< 4%	2 TO 7%	>30,000 PPM	262
10A	< 4%	> 7%	4-10 PPM	6
10B	< 4%	> 7%	11-35 PPM	8
10C	< 4%	> 7%	36-100 PPM	7
11A	< 4%	> 7%	101-3,300 PPM	-9
11B	< 4%	> 7%	3,301-10,000 PPM	-3
12A	< 4%	> 7%	10,001-30,000 PPM	14
12B	< 4%	> 7%	>30,000 PPM	24

2.5 - Membrane-Based CO₂ Removal

The market segment for the DOE CO₂ polymer membrane program is associated or non-associated gas with N₂ less than 4%, H₂S less than 4 ppm, and CO₂ greater than 2%. Polymer membranes simultaneously dehydrate and sweeten gas so that it meets pipeline specifications (4-7 lb H₂O/MMSCF, generally 2% CO₂) without any subsequent treatment.

A subset of Table 2-7, the amount of target gas (N₂ <4%, H₂S <4 ppm, CO₂ >2%) produced is shown in Table 2-8. Annual gas production in the 2-7% CO₂ range is expected to increase significantly. The second section in Table 2-7 shows that annual production of high concentrations of CO₂ (>7%) will increase by 210 BSCF between 1991 and 2000.

Figure 2-4 shows the distribution of all U.S. wells with N₂ <4%, H₂S <4 ppm, and CO₂ from 2-50% per the DOE GASIS database. The ~300 wells identified in the GASIS database include the San Juan, Foreland, and MAFLA regions, as well as other sections of the country. Assuming the GASIS database is representative of the regions of interest, about 30% of the wells are shut in. For the producing wells, Figure 2-4 shows that the average production rate is 10 MMSCFD. Depending on the remoteness of the wells, it may be feasible to develop a market for on-site membrane systems as an alternative to gathering these wells for treatment in a field plant.

Because one option for off-specification CO₂ gas is blending in the pipeline, the Year 2000 production of gas that requires no treatment (N₂ <4%, H₂S <4ppm, CO₂ <2%) is shown in the third section of Table 2-7. Generally, the regions with high CO₂ gas show that 50-90% of the total gas production will require acid gas treatment and/or nitrogen rejection. Generally larger plant sizes are required for reasonable economies of scale where H₂S and nitrogen rejection are required. It is possible that these larger plants could absorb some of the CO₂ processing requirements.

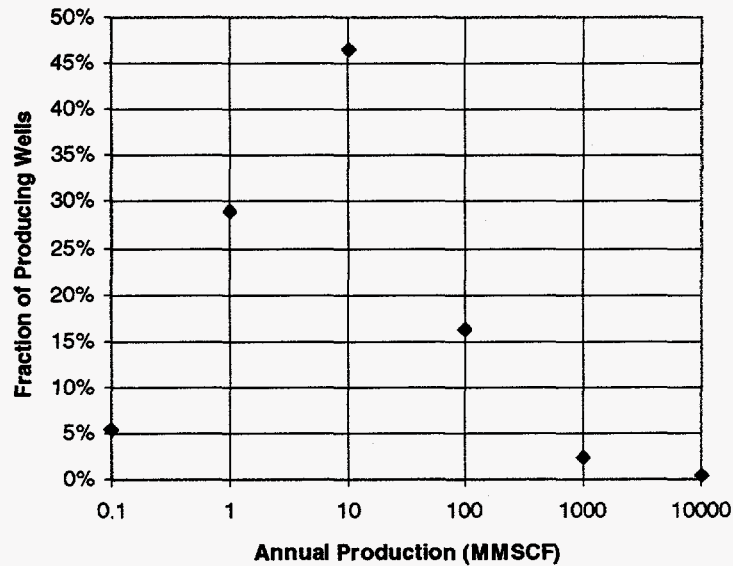
The U.S. currently has about 20% excess acid gas plant capacity, although many of the plants are in regions such as the Permian, with declining production. The predominant process for CO₂-only removal is amine scrubbing, although membrane units were undoubtedly under-reported in the study. (Note that the physical solvents are H₂S selective, implying H₂S and CO₂ removal, while the scavenging processes generally indicate H₂S-only removal.) The amine plants average 90 MMSCFD. Depending on the number of stages and polymer type, membranes are projected to be competitive with amine units at capacities up to 50-90 MMSCFD. Two possible markets for membranes are incremental expansions to the amine plants and smaller units, either at the well site or as small field plants.

Significant gas processing infrastructure will be required for the high-growth CO₂ regions. The 2-7% CO₂ market segment will grow at 44 BSCF/year, requiring an annual gas processing capacity addition of 120 MM SCFD/year. There is evidence that new plants are being built. For example, in Michigan's Antrim region, a 60-MMSCFD amine-based plant was recently built, and Separex sold a two-stage membrane unit. GRI notes 200-MMSCFD incremental expansion plans for three locations in 1996 and 1997, as well as an additional 700-MMSCFD pipeline expansion planned in 1996.

Table 2-8 - Summary of CO₂ Membrane Target Gas Changes by Hydrocarbon Region (Volumes in BSCF/year)

Lower-48	
N₂ <4%, H₂S <4ppm, Carbon Dioxide 2 TO 7%	
1991 Production (BSCF)	1,155
2000 Production (BSCF)	1,520
Change (BSCF)	365
Change %	32%
N₂ <4%, H₂S <4ppm, Carbon Dioxide >7%	
1991 Production (BSCF)	266
2000 Production (BSCF)	488
Change (BSCF)	222
Change %	83%
Gas Requiring No Treatment, N₂ <4%, H₂S <4ppm, Carbon Dioxide <2%	
2000 Production (BSCF)	12,736
Total Gas	
2000 Production (BSCF)	19,122

Figure 2-4 - Distribution of Annual Production for U.S. Gas Wells with N₂ <4%, H₂S <4ppm, and CO₂ from 2-50%, excluding Shut-In Wells



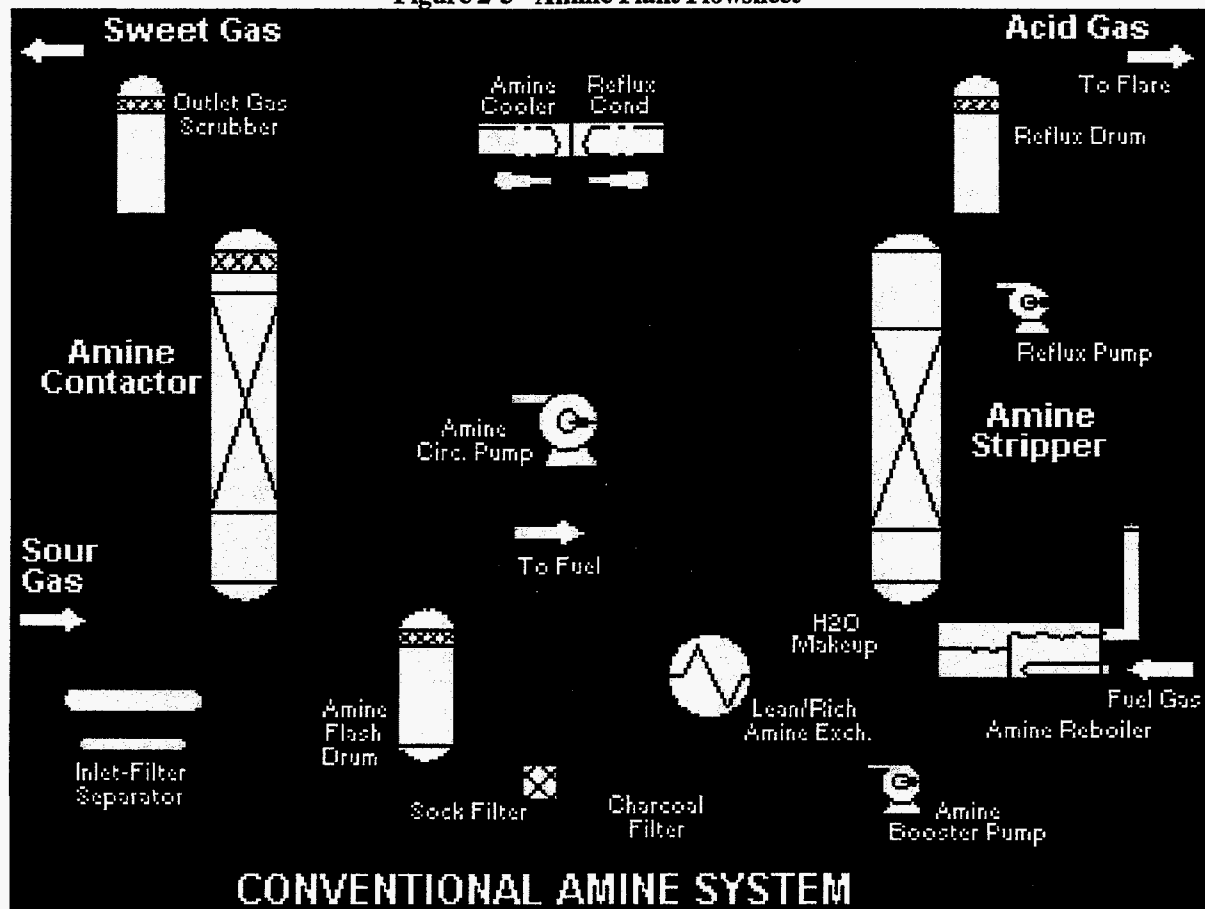
2.6 Technical and Economic Evaluation of Current Processes

2.6.1 Solvent-Based Processes

Currently, there are at least nine different amine-type solvent processes for CO₂ removal. The solvents differ in their stability, regeneration energy requirements, vapor pressure, and selectivity for H₂S over CO₂. In addition to amine-based processes, there are four variations on the Hot Potassium Carbonate process and miscellaneous chemical solvents. Several physical solvents and mixtures of chemical and physical solvents are more commonly used where H₂S is selectively removed from CO₂.

A simplified process flow diagram for solvent systems is shown in Figure 2-5. Although labeled for DEA, the flowsheet is identical for other amines, physical solvents, and mixtures of physical and chemical solvents. The inlet gas enters the bottom of the contactor and flows countercurrently to the solvent. Treated gas leaves the top of the contactor and passes through the outlet gas scrubber, where any solvent that is carried over is removed. The gas is saturated with water and is dehydrated, typically in a glycol unit, then further processed for natural gas liquids recovery or sent directly to the interstate pipeline. The rich solvent leaves the contactor and is flashed to recover hydrocarbons. Rich solvent is preheated in the lean/rich amine exchanger and enters the top of the stripper. Steam generated in the reboiler strips acid gas from the solvent. The acid gases are sent for disposal to the flare or Claus plant, and the lean solvent is returned to the top of the contactor.

Figure 2-5 - Amine Plant Flowsheet¹⁹



Membrane processes have been used for CO₂ removal from natural gas to a limited extent. Their primary use has been in CO₂ recovery from the associated gas in enhanced oil recovery fields. In this application, the CO₂ concentration is greater than 50%, although the total pressure may be only several hundred psi. In contrast, the U.S. natural gas market would more likely have CO₂ concentrations less than 10%, with total pressures up to 1200 psi.

Several emerging technologies will be competing with traditional solvents and membranes. GRI has supported tests of N-Formyl morpholine at Shell's south Texas Fandango gas plant by the Institute of Gas Technology. Preliminary results indicate a 25% overall cost advantage compared to physical solvent processes. Exxon's Controlled Freeze Zone (CFZ) process has been extensively studied for the Natuna gas field, and IFT has successfully marketed its methanol-based system for offshore North Sea gas.

Acid gases (CO_2 and H_2S) are typically removed from natural gas by a regenerative process that uses one of the solvents from the family of alkanolamines, including aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanol amine (MDEA). While many solvents are available, DEA remains the most widely used solvent for CO_2 removal from natural gas. DEA is normally used in concentrations from 20 to 35 wt %. It is contacted at ambient temperature and inlet pressure, and regenerated at a higher temperature and low pressure.

A detailed description of the process, using the flow diagram shown in Figure 2-5, follows. The feed gas passes through an inlet filter separator where entrained droplets of liquid are removed from the gas stream. Typical contaminants in natural gas streams include liquid hydrocarbons, salt water, sands, well-treating compounds and other treating chemicals. Typically a series of sock filters is used with progressively higher capture efficiencies. Material selection for the filters can be critical to avoid contamination of the solvent.

The inlet gas, freed of entrained liquids, enters the bottom of the amine contactor, and the lean amine (35 wt % DEA) enters the top of the contactor. Depending on the size of the contactor, it may have either sieve trays or valve trays, or a section of pall ring packing. The gas passes up from underneath the trays or through the packed section, where nearly all absorption of the CO_2 and H_2S takes place. The treated gas leaves the top of the contactor and passes through the outlet gas scrubber, where any solvent that is carried over is removed. Typically makeup water is sprayed above the top few trays to cool the gas, condensing amine vapors and scrubbing them out of the product gas. The material of construction is carbon steel.

The rich DEA stream leaves the contactor and goes to the amine flash tank to recover hydrocarbons that may have dissolved or condensed in the amine solution while in the contactor. The pressure of the solution is dropped to 100 psia as it enters the tank, allowing the lightest of the hydrocarbons and some of the CO_2 to flash. The flash gas is sent to the fuel gas system. The rich DEA is drained from the bottom of the flash tank and then passed through a 10-micron sock filter for particulate removal, followed by a carbon filter to remove chemical contaminants such as entrained hydrocarbons and surface-active compounds. Continuous cleanup is critical to remove amine degradation by-products, which can cause corrosion, and impurities, which cause foaming.

The rich DEA is then preheated to 220°F in the lean/rich amine exchanger by exchanging heat with the lean DEA exiting the amine booster pump, thereby reducing the heat load on the amine reboiler. It is important to avoid temperatures higher than 220°F to prevent degrading the amine, which leads to corrosive by-products. Often higher corrosion-resistant metals are specified for the lean/rich exchanger.

Like the contactor, the amine stripper also has sieve or valve trays, or a packed section. The preheated rich DEA enters the top of the stripper, which operates at a pressure of 30 psia, and flows down countercurrently to a gas stream of steam and acid gas. The steam is generated in the amine reboiler. The reboiler can be direct-fired, but this can result in hot spots and corrosion; heating the DEA against low-pressure steam is preferred.

The overhead gas is passed through a reflux condenser to recover water and the small amount of amine that is vaporized in the stripper. The condensed liquids are pumped from the reflux accumulator back to the top of the stripper as reflux by the reflux pump. The acid gases are sent for disposal to the flare or to a sulfur recovery unit if H_2S is sufficiently high to require emission control.

Lean DEA solution from the bottom of the amine reboiler is pumped by the amine booster pump through the lean/rich amine exchanger before going to the amine circulating pump. When necessary, amine and water makeup are added to the lean amine from drums or storage tanks. The lean DEA is then pumped through the lean amine cooler back to the amine contactor to complete the process loop.

Purvin and Gertz give capital and operating costs for DEA plants as a function of capacity (MMSCFD) and CO_2 concentration. The costs are similar for H_2S systems, although combined $\text{H}_2\text{S}/\text{CO}_2$ systems deviate slightly due to the thermodynamics of absorption. With these costs it is possible to estimate the value of the SSF system. The

capital costs, which include start-up (two months operating expense), initial supplies, minimum spare parts, and sales taxes, but exclude land, interest during construction and insurance, are:

$$\begin{aligned} \text{log cost (MM 1992\$)} = & -1.154 + 0.276*\ln(\text{Inlet mol\% CO}_2) \\ & + 0.64*\log(\text{MMCFD capacity}) \end{aligned} \quad (1)$$

Capital costs for the contactor tower are affected by the volume of gas to be treated, the concentration of CO₂ in the inlet gas, and the pressure of the gas. The cost of the regeneration section is primarily affected by the circulation rate of the DEA solution, which is determined by the volume of CO₂ to be removed.

Operating costs, which include labor (and 25% for benefits), taxes, insurance, electricity at \$0.06/kWH, and 15% contingency, but exclude fuel, are:

$$\begin{aligned} \text{Operating cost (\$/MMBTU, 1992\$)} = & (0.08 + .2*\text{acid gas concentration}) \\ - & (0.026 + 0.22*\text{acid gas concentration})*\log \text{MMSCFD} \end{aligned} \quad (2)$$

Fuel consumption is a function of DEA loading and the circulation rate. For 30 wt % DEA, the required reboiler duty is 0.11 MMBTU/lbmol acid gas.

Gas that has been treated with amines is saturated with water after exiting the stripping column. Dehydration costs using a glycol system are discussed in Section 6.1, and generally range from \$0.02-0.05/MMSCF.

2.6.2 Membrane-Based Processes

GRI has published a series of reports on its tests of a Grace cellulose acetate membrane at Dallas Production, Inc. in East Texas. Air Products' Corporate Science and Technology department (CSTC) has screened several classes of polymers for CO₂/CH₄ separations, and has concluded that single- or dual-stage membrane systems using MEM1 may be competitive with DEA (see Section 4). The critical issues for membrane systems are high hydrocarbon losses and poor life due to fouling or chemical attack.

The capital, operating, and methane slippage costs for single- and dual-stage MEM1 and GDX membranes in CO₂ removal service for natural gas are detailed in Section 4. For a 35-MMCFD facility reducing 7% CO₂ gas to 2%, a two-stage MEM1 membrane unit appears competitive with DEA. The membrane simultaneously dehydrates and sweetens the gas. Note that CO₂ removal will usually dictate membrane area, so the gas is drier than required. Selectivity, or reducing methane losses, is the key issue in making membranes competitive. Customers, including Shell, Chevron, and Unocal, have expressed concern regarding membrane life, particularly under atypical operating conditions that can slug the membrane with brine, condensate, drilling mud, etc. As part of this program, Air Products is performing bench-scale challenge tests to assess membrane life issues, to be followed with field tests (see Section 4).

Several configurations were assessed. Table 2-9 compares total life cycle costs for single-stage MEM1 and GDX membranes to conventional cellulose acetate membranes (based on published GRI values), and to DEA/glycol trains (based on Purvin and Gertz economics).

Table 2-9 - Summary of GDX MEM1 Membrane Relative Costs versus Alternative Processes
Gas Value = \$2/MMBTU

Process Configuration	GDX Membrane		MEM1 Membrane		Other Technologies	
	Single Stage	Two-Stage MEM1	Single Stage	Two-Stage GDX	Single-Stage Cellulose Acetate Membrane	DEA/Glycol
Methane Loss	1.1482	0.1445	1.2260	0.1247	1.8232	0.2215
Capital	0.1629	0.3742	0.2649	0.5121	0.0939	0.3749
Annual Operations	0.1101	0.2480	0.1688	0.3294	0.1363	0.4035
Total	1.4212	0.7667	1.6597	0.9662	2.0514	1.0000

Because methane losses dominate the economics for all the single-stage membrane systems, a two-stage GDX or MEM1 was considered the best option for the North American market, where wellhead methane is valued at \$2/MMBTU. However, lower gas pricing accentuates the low-capital advantage for single-stage MEM1 or GDX, resulting in a relative total cost of 0.734 compared to 0.836 for glycol (at \$0.5/MMBTU). Consequently there may be a fit for polymeric membranes where capital and methane losses carry different weights.

Appendices to Chapter 2

Table A1 - Major Natural Gas Producers

Rank in 1990 by Production	Company	Affiliated Companies
1.	Chevron Oil & Gas USA	Warren
2.	Texaco, Inc.	
3.	Exxon	
4.	Amoco Production Co.	
5.	Mobil Oil Corp.	
6.	Arco Oil & Gas	
7.	Shell	
8.	Unocal	
9.	Phillips Petroleum Co.	
10.	Marathon	
11.	Oryx	
12.	Conoco	
13.	Occidental	
14.	Meridian Oil Hydrocarbons	
15.	Union Pacific Resources	
16.	Amerada Hess	
17.	BP Oil Company	
18.	Enron Gas Liquids Co.	Northern Natural
19.	Anadarko	
21.	Mesa Petroleum	
22.	Pennzoil	
23.	Southern Natural Gas Company	
24.	Maxus Exploration Co.	
25.	Apache	
26.	Coastal	
27.	Kerr McGee Corp.	
28.	Enserch Processing	Enserch Exploration
30.	Union Texas	
32.	Murphy Oil	Ocean Drilling
33.	Columbia Gas	
34.	Freeport-McMoran Oil and Gas	
35.	Nerco	
36.	Endevco Nat. Gas Co.	Clairborne, Dubach
38.	Arkla Gas Co.	
39.	Mitchell Energy	Liquid Energy
40.	Louisiana Land & Expl.	
42.	BHP Petroleum	
43.	Pacific Enterprises	
44.	American Oil & Gas	Cabot, Maple
45.	Questar	
47.	Pogo Producing	
48.	Santa Fe Energy	Santa Fe Partners
49.	Diamond Shamrock	
56.	Mountain Gas Resources	
57.	AMAX Oil & Gas	
67.	Seagull Energy	
78.	Parker & Parsley	Damson
79.	Torch Energy Marketing	Nuevo

Table A2 - Historical U.S. Natural Gas Production; Volumes Reported in MMSCF and Average Wellhead Price Reported in \$/MSCF (not adjusted for inflation) (13)

Year	Gross With-drawals	Used for Repressur- ing	Nonhydro- carbon Gases Removed	Vented and Flared	Marketed	Production Extraction Loss	Dry Production	Average Wellhead Price
1970	23,786,453	1,376,351	NA	489,460	21,920,642	906,413	21,014,229	0.17
1971	24,088,031	1,310,458	NA	284,561	22,493,012	883,127	21,609,885	0.18
1972	24,016,109	1,236,292	NA	248,119	22,531,698	907,993	21,623,705	0.19
1973	24,067,202	1,171,361	NA	248,292	22,647,549	916,551	21,730,998	0.22
1974	22,849,793	1,079,890	NA	169,381	21,600,522	887,490	20,713,032	0.30
1975	21,103,530	860,956	NA	133,913	20,108,661	872,282	19,236,379	0.44
1976	20,943,778	859,410	NA	131,930	19,952,438	854,086	19,098,352	0.58
1977	21,097,071	934,801	NA	136,807	20,025,463	862,563	19,162,900	0.79
1978	21,308,815	1,181,432	NA	153,350	19,974,033	852,130	19,121,903	0.91
1979	21,883,353	1,245,074	NA	167,019	20,471,260	807,845	19,663,415	1.18
1980	21,869,692	1,365,454	199,063	125,451	20,179,724	776,605	19,403,119	1.59
1981	21,587,453	1,311,735	221,878	98,017	19,955,823	774,562	19,181,261	1.98
1982	20,272,254	1,388,392	208,492	93,365	18,582,005	761,942	17,820,063	2.46
1983	18,659,046	1,458,054	221,937	94,962	16,884,093	789,632	16,094,461	2.59
1984	20,266,522	1,630,152	224,118	107,913	18,304,339	837,867	17,466,472	2.66
1985	19,606,699	1,915,197	326,497	94,778	17,270,227	816,370	16,453,857	2.51
1986	19,130,711	1,837,552	336,851	97,633	16,858,675	799,645	16,059,030	1.94
1987	20,140,200	2,207,559	376,033	123,707	17,432,901	812,320	16,620,581	1.67
1988	20,999,255	2,478,382	459,883	142,525	17,918,465	815,844	17,102,621	1.69
1989	21,074,425	2,475,179	362,457	141,642	18,095,147	784,502	17,310,645	1.69
1990	21,522,622	2,489,040	289,374	150,415	18,593,792	784,118	17,809,674	1.71
1991	21,750,108	2,771,928	275,831	169,909	18,532,439	834,637	17,697,802	1.64
1992	22,132,249	2,972,552	280,370	167,519	18,711,808	871,905	17,839,903	1.74
1993	22,725,642	3,103,014	413,971	226,743	18,981,915	886,455	18,095,460	2.04
1994	23,580,706R	3,230,667 R	412,178	228,336 R	19,709,525 R	888,500	18,821,025	1.85
1995	23,743,628	3,565,023	388,392	283,739	19,506,474	907,795	18,598,679	1.55

R = Revised data.

NA = Not available.

Notes: Beginning with 1965 data, all volumes are shown on a pressure base of 14.73 psia at 60 degrees Fahrenheit. For prior years, the pressure base is 14.65 psia at 60 degrees Fahrenheit.

Sources: 1930-1975: Bureau of Mines, Minerals Yearbook, "Natural Gas" chapter. 1976-1978: Energy Information Administration (EIA), Energy Data Reports: Natural Gas.

Annual. 1979: EIA, Natural Gas Production and Consumption, 1979. 1980-1995: EIA, Form EIA-627, "Annual Quantity and Value of Natural Gas Report"; Form EIA-176,

"Annual Report of Natural and Supplemental Gas Supply and Disposition"; Form EIA-64A, "Annual Report of the Origin of Natural Gas Liquids Production"; and Form EIA-816,

"Monthly Natural Gas Liquids Report."

Table A3 - U.S. Natural Gas Reserves by State/Region

State or Region	Reserves (BSCF)
Alaska	9,733
Lower 48 States	154,104
Alabama	4,830
Arkansas	1,607
California	2,402
Coastal Region Onshore	194
Los Angeles Basin Onshore	103 6
San Joaquin Basin Onshore	2,044
State Offshore	61
Colorado	6,753
Florida	98
Kansas	9,156
Kentucky	969
Louisiana	9,748
North	2,537
South Onshore	6,251
State Offshore	960
Michigan	1,323
Mississippi	650
Montana	717
New Mexico	17,228
East	3,021
West	14,207
New York	242
North Dakota	507
Ohio	1,094
Oklahoma	13,487
Pennsylvania	1,800
Texas	35,974
RRC District 1	703
RRC District 2 Onshore	1,360
RRC District 3 Onshore	3,366
RRC District 4 Onshore	7,547
RRC District 5	2,011
RRC District 6	5,381
RRC District 7B	425
RRC District 7C	3,316
RRC District 8	5,442
RRC District 8A	1,219
RRC District 9	728
RRC District 10	4,246
State Offshore	230
Utah	1,789
Virginia	1,833
West Virginia	2,565
Wyoming	10,879
Federal Offshore a	28,388
Pacific (California)	1,170
Gulf of Mexico (Louisiana)a	20,835
Gulf of Mexico (Texas)	6,383
Miscellaneous b	65
U.S. Total	163,837

Table A4 - Summary of Natural Gas Construction Activity

	NG Plant Projects*				<u>Gas Treating</u>	<u>N₂ Removal</u>	<u>Amine Treater</u>	<u>NGD</u>
	<u>new</u>	<u>MMSCF</u>	<u>expand.</u>	<u>MMSCF</u>				
U.S.	9	1862	6	>150	7 (2#)	5	2	
Canada	20	620	7	>800	-		3	1
Central & S Amer.	6	1826	4		2 (2#)	-	3	
Europe	5	>2655	0		7 (2#)	-	6	
Africa & Mid East	6	5260	3		4	-	5	6
Far East	10	1659	0		10 (7#)	-	2	7
Australasia	2	250	4		6 (1#)	-	1	
WW totals	58	14,132	24		36 (14#)	5	22	14

* may also include unstated CO₂ and / or H₂S removal equipment

specified as CO₂ removal projects

Table A5 - Compiled Projects in Natural Gas - New Plants, Revamps, AGR Needs

United States

<u>Company</u>	<u>Location</u>	<u>Project</u>	<u>Size</u> <u>(MMSCFD)</u>	<u>Status</u>	<u>Est \$</u>	<u>E&C</u>
Thums Long Beach	Long Beach, (CA)	NG Plant	10	C97	3	Propak
Torch Energy	Lompoc (CA)	NG Plant	15	C97		Propak
		Amine Treater	15	C97		Propak
Union Pacific Resources	Cheyene Wells (CO)	NG Plant	35	P		
		N ₂ Removal		E98		PSI
Amoco Prod. Co	Grant Co (KA)	NG He,	450	U98		Randall
		N ₂ Removal				
Mesa Operating	Ulysses (KA)	N ₂ Removal	220	E98		
Bridgeline Gas Dist	Larose (LA)	NG Plant	to 600	U98	92	BVPI/Randall
	Paradis	NG Plant	+125	U97	5	Staff/Pillerin
Union Pacific Resources	Vernon Parish (LA)	NG Plant	100	U97		Schedule A
Conoco	Lake Charles (LA)	Treater, Amine		C		Raytheon
CMS Transmission	Otsego (MI)	CO ₂ Removal	70	C97		Russell
Amoco	Pascagoula	NG Plant	1000	E99		Bechtel/Becon
Western Gas Resources	San Juan Co (NM_	NG Plant	17	E98		Staff
Texaco Producing Co	Hobbs	CO ₂ Removal		E97		Randall
Delhi Gas Pipeline	Freestone Co (TX)	AGR	by 150	P98		
	Robertson Co (TX)	AGR	50	E97	2.2	Staff
Mesa Operating	Amarillo (TX)	NG Plant, N ₂ Removal	to 140	U	4.0	
Producers Operating Co	Clay Co (TX)	N ₂ Removal	10	U97		Schedule A
Rockland Pipeline Co	Freestone Co (TX)	Gas Treating		C97		Russell
Valero Hydrocarbons	Hidalgo Co (TX)	NG Plant	125	P97		
Western Gas Resources	Anderson Co (TX)	AGR	200	C97		Staff
		AGR	to 350	E97		
	Midland Co (TX)	NG Plant	100	P98		
	Pecos Co (TX)	AGR	re 80	E98		
	Regan Co (TX)	NG Plant	to 45	C97		
Louisiana Land & Explor	Fremount Co (WY)	NG Plant	by 11	E98	6	Raytheon
Western Gas Resources	Converse Co (WY)	NG Plant	to 30	E98		Staff

Canada

<u>Company</u>	<u>Location</u>	<u>Project</u>	<u>Size</u> <u>(MMSCFD)</u>	<u>Status</u>	<u>Est \$</u>	<u>E&C</u>
Alberta Energy	Clairmont (AL)	NG Plant	20	U98	6.0	Titan
	Fontas (AL)	NG Plant	by 20	U98	5.0	Titan
Anderson Exploration	Cecil (AL)	NG Plant	42	P98	9.3	Gas Liquids
	Normandville	NG Plant	15.0	U97	10.0	Gas Liquids
Anderson Oil Services	Normandville	NG Plant	15.0	U97	0.6	Propak
Blue Range Resources	Chinchaga	NG Plant	15.0	U97	1.4	Gas Liquids
Cabre Exploration	Kessler	NG Plant	18.0	E97	3.1	Gas Liquids
Canrise Resources	McLeod River	NG Plant	15.0	E97	2.2	Gas Liquids
Can Rock Pipeline	Fourth Creek	NG Plant	53.0	C97	15.0	Gas Liquids
		NG Plant	20.0	U97	0.7	Propak
		Treater, Amine	15.0	U97	0.6	Propak
Chauvco Resources	Wayne (AL)	NG Plant	10	U97	0.3	Propak
Compton Resources	Gladys Ridge (AL)	Treater, Amine	156	U97	0.6	Propak
Inuvialuit	Haro (AL)	NG Plant	by 8.0	U97	1.5	Gas Liquids
New Cache Petroleums	Ft. Assiniboine (AL)	NG Plant	18	U97		Stanley
Numac Energy	Martins Creeks (AL)	NG Plant	30.0	C97	7.0	Gas Liquids
	Rob (AL)	NG Plant	50.0	E97	3.2	Gas Liquids
Ranger Oil	Parkland (AL)	NG Plant	to 35.0	C97		Gas Liquids
Roan Resources	Mahaska (AL)	NG Plant	10.0	E97	2.2	Gas Liquids
Saxon Petroleum	Bigory (AL)	NG Plant	10.0	C97	0.6	Propak
Wolcott Gas Processing	Empress (AL)	NG Plant	by 425	E99		Prowest
Canadian Hunter Expl.	Ring (BC)	Treater, Amine	8.0	U97	0.6	Propak
Novagas Canada	West Stoddart (BC)	NG Plant	120.0	E98	60.0	Delta Hudson
Penn West Pet..	Firebird (BC)	NG Plant	8.0	C97	36.0	Gas Liquids
Penn West Pet.	Wildboy (BC)	NG Plant	40.0	P98	10.0	
Rigel Oil and Gas	Boundary Lake (BC)	NG Plant	by 35.0	C97	2.0	Titan
Solex Gas Liquids	Taylor (BC)	NG Plant	by 320.0	U98	22.5	Pro West
Westcoast Gas Services	Ft. St. John (BC)	NG Plant	ex 80.0	C97	51.0	Kavaerner
	"	NG Plant	110.0	C97	43.0	Pro West
Tri Link Resources	Estevan	NG Plant	1.0	E97	-	Stanley

Central and South America

<u>Company</u>	<u>Location</u>	<u>Project</u>	<u>Size</u> <u>(MMSCFD)</u>	<u>Status</u>	<u>Est \$</u>	<u>E&C</u>
Amoco Argentina	Yac Bayo (Argen)	NG Plant	10.6	C97	-	Tecna
Filo Morado	Buenos Aires (Argen)	NG Plant	70.0	E98	12.0	Pro Quip
Pluspetrol Expl & Prod	Neuquen (Argen)	NG Plant	re 45.0	E97		Kti Fish
Petr Brasileiro	S Francisco Sul (Brazil)	NG Plant	34.8	P	-	Petrobras
Sipetrol	Secoya (Ecuador)	NG Plant	to 5.0	C97	8.0	Petroindl/Propak
Halliberton Energy Ser.	Chiapas (Mexico)	CO ₂ Removal	138	U97	-	(UOP)
Petroleos Mexicanos	Cactus (Mexico)	NG Plant	ex 600.0	C97	-	Fluor Daniel
		NG Plant	ex 100.0	U97	-	Fluor Daniel
		NG Plant	600.0	E98	-	Fluor Daniel
	Nuevo Pemex (Mexico)	NG Plant	600.0	U98	-	-
	Reynosa (Mexico)	Treater, Amine	5.0	E98	1.1	Propak
	Tula	Treater, Amine	0.3	U97		Snamp/TPA
Phoenix Park Gas Process.	Ponit Lisas (Trinidad)	NG Plant	500.0	E98	40.0	BVPI
Posven CA	Puerto Ordaz (Venez.)	CO ₂ Removal	-	U98	-	(UOP)
Corpoven	Puerto La Cruz (Venz)	Treater, Amine	14.5	P		IFP

Europe

<u>Company</u>	<u>Location</u>	<u>Project</u>	<u>Size</u> <u>(MMSCFD)</u>	<u>Status</u>	<u>Est \$</u>	<u>E&C</u>
OMV AG	Aderklaa (Austria)	NG Plant	ex	U97		German Linde
Distrigas	Loenhof (Belgium)	Nat gas Treating				KCC
Amoco UK Ltd	Tesside (England)	NG Plant	600.0	U97	1.0.	Parsons
		NG Plant	600.0	U98		Parsons
DEA Mineraloel	Heide (Germany)	Treater, Amine		E		Lurgi
Agip	Val D'Agri (Italy)	Gas Treating	35.0 t/d	E98	17.5	Shell
IPLOM	Priolo Gargallo	AGR	328	U99		Snampr. (DOW)
Ned Aadolie	Griupskerk (Nether.)	Gas Treating	-	U97		Lummus
Shell Neth.	Pernis (Nether.)	Treater, Amine	450 t/d	E97		Comprim/SIRM
Statoil	Sleipnervest (Norway)	Nat Gas Treat.	942.0	U		Kvaener/E. Aquitane
Petrochemia Plock	Plock (Poland)	Treater, Amine		C97		Snamprog/UOP
Polish Oil and Gas	Debno (Poland)	NG Plant	55.0	U98	52.0	Propak
Petrtel SA	Ploiesti (Romania)	Treater, Amine	re	P	3.6	IPIP/UOP
Angarsk Petrochemi	Angarsk (Russian Fed)	Treater, Amine	42.0 Mt/y	P		
Nyas AB	Nymashamn (Sweden)	Treater, Amine	480.0 t/d	E99	40.0	TecPet/Comprim
Dneprodzershzin	Dneprodzershzin	CO ₂ Removal	1.0 Mt/d	U97		UCSA
		CO ₂ Removal	1.0 Mt/d	U97		
Powergen	Conah's Quay	NG Plant	200.0	U		Costain

Africa and Middle East

<u>Company</u>	<u>Location</u>	<u>Project</u>	<u>Size</u> <u>(MMSCFD)</u>	<u>Status</u>	<u>Est \$</u>	<u>E&C</u>
Sonatrach	Hasi Messaoud (Algeria)	NG Plant	re	U		JGC
Amerya Petr. Ref	Amerya (Egypt)	Treater, Amine		U97	1.4	Propak
Khalda Petro	Cairo (Egypt)	NG Plant	165	E98		KTI Fish
Middle East Oil Ref	Amerya (Egypt)	Treater Amine		E		Technip/T Petrol
	Amerya (Egypt)	Treater Amine		E		Technip/T Petrol
Nigeria LNG Co	Bonny Island (Nigeria)	Nat Gas Treating	897	E97		Technip/ E Aqui
National Iran Oil Co	(Iran)	Treater, Amine		U98		Chiyoda
	(Iran)	Treater, Amine		U98		Chiyoda
Kuwait Natl Petr.	Mina al Ahmadi	Gas Treating	200.0	E99		SKEC
Petr Dev Oman	Saih Rawl (Oman)	Gas Treating	990.0	E99		Snamprogetti
Qatar Liquified Gas	Ras Laffin (Qatar)	NG Plant	970.0	C	110.0	TEC
Saudi Aramco	Abqaiq (Saudi Arabia)	NG Plant		E98		Technip
	Hawiyah (Saudi Arab)	NG Plant	1600	E		Parsons
	Shedgum (Saudi Arab.)	NG Plant	ex 400.0	E99		BVPI
	Uthmaniyah (SA)	NG Plant	600.0	E98		Parsons
Abu Dhabi Natl Oil CO	Asab Field (UAE)	NG Plant	825	E99		BVPI
	Habshan (UAE)	NG Plant	1100	E99		Technip
	Taweelah	Gas Treating	640.0	E		KJB

Far East

<u>Company</u>	<u>Location</u>	<u>Project</u>	<u>Size</u> <u>(MMSCFD)</u>	<u>Status</u>	<u>Est \$</u>	<u>E&C</u>
Occidental Co Bangladesh	Lakatura (Bang)	NG Plant	125.0	E98		Titan/KJB/IFP
Sylhet Gas Fields Limited	Rishidpour (Bang)	NG Plant	90.0	P98		Titan
China Nat'l Machinery	Tianjin (China)	NG Plant	40.0	E		Proquip
China petr Tech & Dev	Tar Zhong (China)	NG Plant	60.0	U97		German Linde
Chishui Nat Gas & Chem	Chishui (China)	CO ₂ Removal	1.6 Mt/d	C97		UCSA
Daqing Petr	Daqing	Gas Treating	42.0	E		Pro Quip/ IFP
Nanjing Chemi Ind	Nanjing (China)	AGR	122.0	U98		German Linde
Shanghai Petr. Complex	Shanghai (China)	NG Plant	57.0	U98	11.9	Propak
Shaan-Xi Chemi Fert	Xian (China)	CO ₂ Removal	23.3	E99		Sixth DI/G-V
Wuhu Gas Co.	Wuhu (China)	Gas Treating	7.0	E		LGI
Xin Jiang Chem Fert	Urumqi (China)	CO ₂ removal	7.7	E98		Sixth DI/G-V
Bharat Petr Corp	Mahul (India)	Treater, Amine	1.0 MMt/y	E99		ENG India/UOP
Ind Farmers Fert Coop	Phulpur (India)	CO ₂ Removal	41.0	U97		PDIL Topso/GV
Indian Petrochem	Bombay (India)	NG Plant	280	E98		KTI Fish
Nagarjuna Fert & Chem	Kakinada (India)	CO ₂ Removal	24.8	U98		G-V
Oil & Nat Gas Comm	Hazira (India)	NG Treating	6.3	C	45.0	Hyundai/E Aquit
Oil India	Jaiselmer	NG Plant	1.0	E	15.0	Triune
Southern Petrochem	Tuticorin (India)	CO ₂ Removal	to 36.5	U98		KTI / G-V
Malaysian Ref.	Melaka	Treater, Amine		E98		Chiyoda
Petronas Gas	Paka (Malaysia)	NG Plant	500.0	U98		Daelim/IJM/Marube
		NG Plant	500.	U98		
Al Noor Fert	Karachi (Pakistan)	CO ₂ removal	to 22.8	E99		CNCEC / G-V
Oil & Gas Dev	Missakesual (Pakist.)	NG Plant	6.0	U97	<8.5	Titan

Australasia

<u>Company</u>	<u>Location</u>	<u>Project</u>	<u>Size</u> <u>(MMSCFD)</u>	<u>Status</u>	<u>Est \$</u>	<u>E&C</u>
BHP DRI Australia	Port Headland (Austr)	CO ₂ Removal	315.0	E97		KTI
Boral Energy Co	Katnook (Australia)	NG Plant	ex	C97	3.0	AMEC/KJB
	Naccowlah (Australia)	NG Plant	40.0	C	10.0	KJB
Santos	Ballera	Gas Treating	by 59.0	E98		KJB
	Ballera	Gas Treating	ex 133.0	C97		KJB
	Ballera	Gas Treating	by 69.0	U97	100.0	KJB
Asamera Overseas	Sumatra(Indon)	NG Plant	210.0	P99	28.0	Titan
Maxus Energy Corp	Offshore (Indon)	Gas Treating	80.0	P97	350.0	Staff
Mobil Corp	Kabing Island (Indon)	Gas Treating	105.0	E98		BVPI
Fletcher Challenge Energy	Kaimiro (NZ)	NG Plant	by 4.0	P98		
Nat Gas Corp New Zealand	Kapuni (NZ)	NG Plant	re 200.0	U97	15.0	Worley
	(NZ)	NG Plant	re	C97	3.5	Worley
Petron Corp	Limay (Philp)	Treater, Amine	6.3 Mb/d	E98		BVPI

Symbols:

- by: increment of capacity added
 - to: total capacity after construction
 - re: revamp
 - ex: expansion; not further classified
 - P: planning
 - E: engineering
 - U: under construction
 - C: completed
- est cost in \$MM U.S.

3.0 Development and Evaluation of Membrane Polymers and Membranes

Summary

GDX hollow-fiber membranes were evaluated for pure gas CO₂ and CH₄ permeability. The results demonstrate that the fiber spun during pilot plant trials was defect repairable to intrinsic selectivity. At 23°C, the CO₂ permeance showed a marked increase at CO₂ pressures above 300 psig, indicating that CO₂ was plasticizing the polymer. This effect was not observed at 50°C, where the CO₂ activity was lower. Additional evidence was found in the CO₂ adsorption isotherms for this polymer. GDX results were compared to a benchmark polymer MEM1, which displayed a lower degree of plasticization at 23°C. Preliminary mixed-gas testing indicated no mixed-gas effects for either GDX or MEM1.

3.1 Evaluation of GDX Test Loops

3.1.1 Permselectivity

The GDX hollow-fiber membrane used in this work was produced as described previously.²¹ It is important to note that the ratio of D/X components was not optimized during the scaleup of this polymer, and therefore the CO₂/CH₄ was less than expected for the optimum material; likewise, the CO₂ permeance was higher than that of the optimum material composition. The membranes utilized in this work consisted of 10-20 individual hollow fibers, about 20 cm in length, sealed into an epoxy tubesheet. The other end of the bundle was epoxied or heat-sealed closed. The tubesheet was sealed into a ½" diameter stainless steel housing. The modules were shell-side fed with pure gas, and the resulting permeate flow out of the bore side was measured on electronic and/or soap film flowmeters. The variables investigated included gas pressure, membrane temperature, and performance stability over time.

Results for the GDX membrane are shown in Figures 3-1 and 3-2. The CO₂ permeance at 23°C was independent of CO₂ pressure up to about 300 psig. At 400 psig, the CO₂ permeance increased markedly, most likely a result of plasticization of the polymer by high-pressure CO₂. As expected, the permeance of pure CH₄ was independent of pressure over this range (Figure 3-2). Thus, the *apparent selectivity* (the ratio of the pure component permeances) increased with increasing CO₂ pressure (Figure 3-5). However, the literature suggests that a mixed gas measurement would show quite different behavior, and that the CO₂/CH₄ selectivity of a CO₂-CH₄ mixed gas system would actually decrease at high CO₂ pressures.

Figure 3-1 - CO₂ Permeance of GDX Test Loops as a Function of Pressure @ 23°C
(PP062896-2)

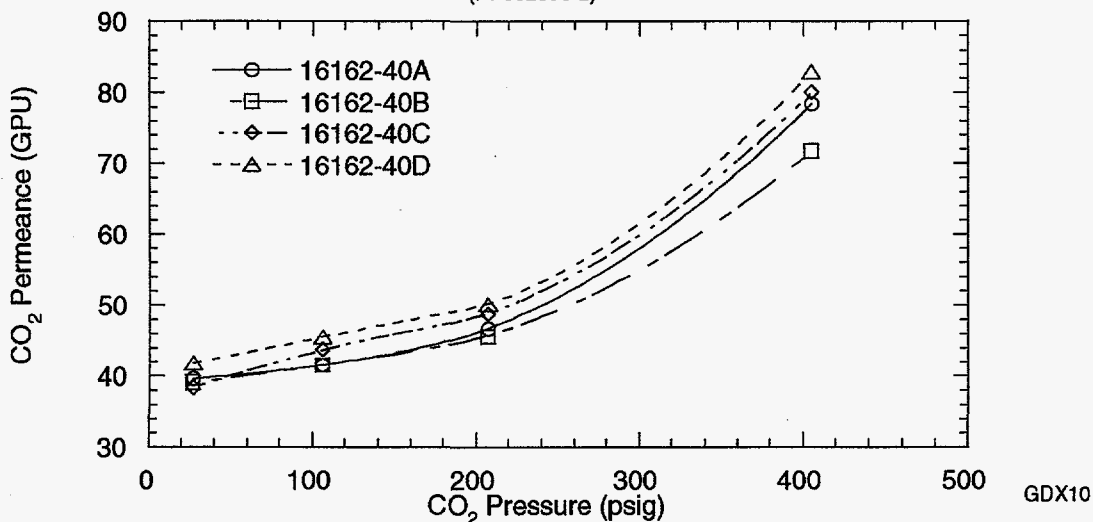
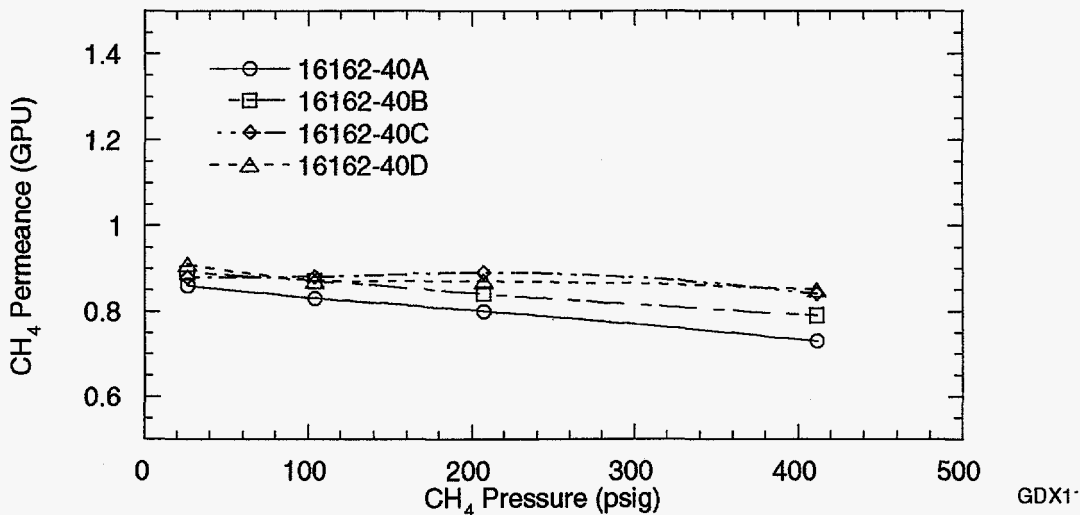


Figure 3-2 - CH₄ Permeance of GDX Test Loops as a Function of Pressure @ 23°C
(PP062896-2)



The CO₂ and CH₄ permeability at 50°C is shown in Figures 3-3 and 3-4, respectively. At 50°C, plasticization was not an issue within this pressure range, and the CO₂ permeance was independent of CO₂ pressure (Figure 3-3). Again, CH₄ permeation was independent of pressure. (The slight decrease in CH₄ permeance at higher pressures may indicate compacting of the membrane.) Consequently, the apparent CO₂/CH₄ selectivity exhibited insignificant pressure dependence at 50°C (Figure 3-5).

Figure 3-3 - CO₂ Permeance of GDX Test Loops as a Function of Pressure @ 50°C

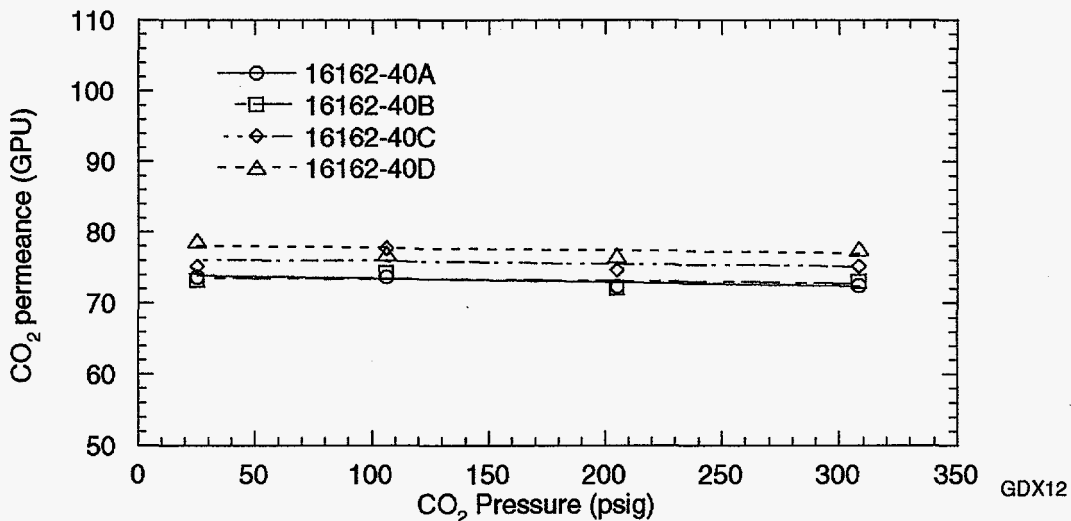


Figure 3-4 - CH₄ Permeance of GDX Test Loops as a Function of Pressure @ 50°C
(PP062896-2)

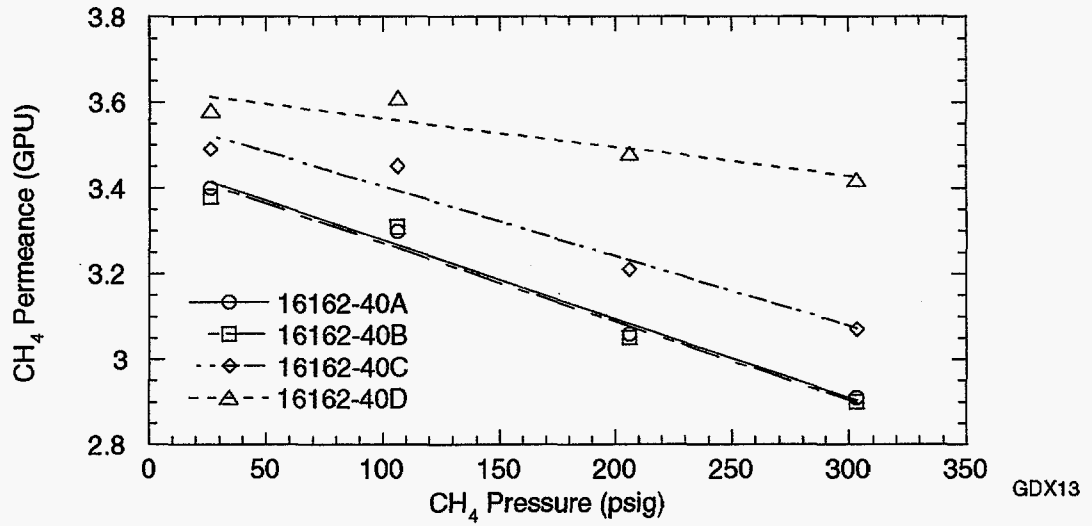
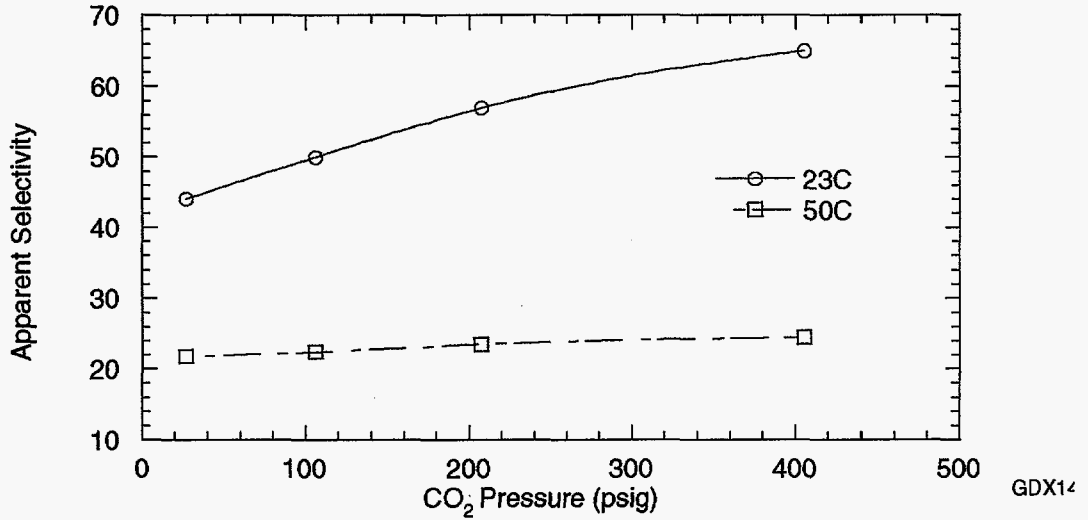


Figure 3-5 - Apparent Selectivity of GDX Test Loops
(PP062896-2)



3.1.2 Adsorption Isotherms

Adsorption isotherms were measured on GDX membranes using a volumetric uptake apparatus. The uptake vs. pressure curve for CH₄ was 'linear'; however, the signal was too noisy to extract a Henry's law coefficient. The isotherms for CO₂ are shown below for 35°C (Figure 3-6) and -10°C (Figure 3-7). At 35°C, the isotherm displayed dual mode behavior, that is, filling of both Langmuir and Henry's Law sites at low pressure (<2 atm) followed by sorption via Henry's Law at higher pressures. The isotherm at 35°C did not exhibit indications of CO₂ plasticization. At -10°C, dual mode behavior was observed up to approximately 15 atm CO₂. Above that region, the slope change indicated CO₂ plasticization.

Figure 3-6 - CO₂ Sorption Isotherms for GDX at 35°C

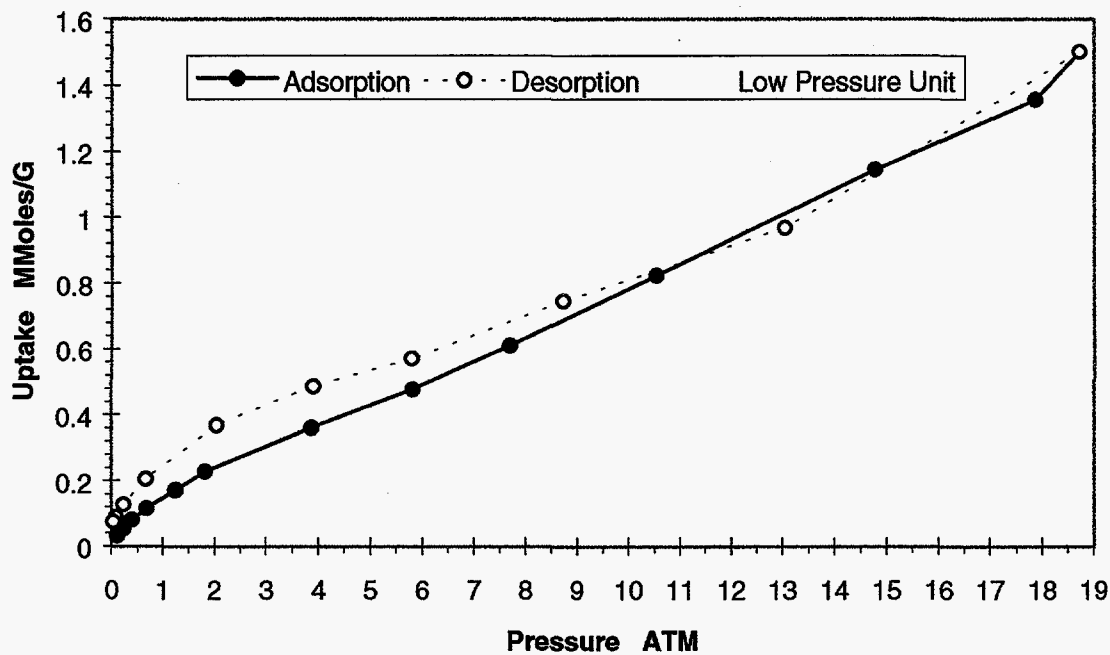
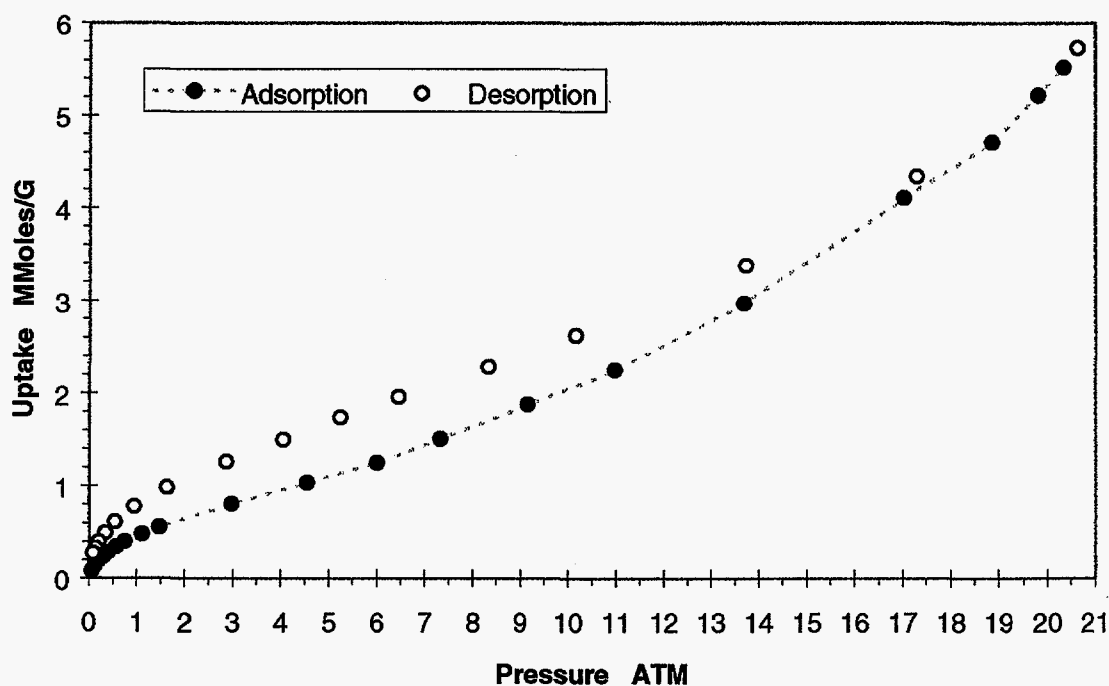


Figure 3-7: CO₂ Sorption Isotherms for GDX at -10°C



3.2 Evaluation of MEM1 Test Loops

3.2.1 Permselectivity

MEM1 test loops were also evaluated as part of benchmarking studies. Figure 3-8 shows how the CO₂ permeance of 4 test loops varied as the CO₂ feed pressure was increased from 25 to 400 psig. The permeance remained relatively constant up to 225 psig; at higher pressure, there was marked increase in CO₂ permeance attributed to plasticization of the polymer. Similar effects have also been observed for other polymer systems.²⁰ Methane, being less condensible, did not exhibit plasticization behavior under these conditions (Figure 3-9). Consequently, the *apparent* CO₂/CH₄ selectivity increased as the CO₂ pressure was increased (Figure 3-10).

Figure 3-8 - CO₂ Permeance as a Function of CO₂ Pressure: MEM1 Membrane @ 23°C

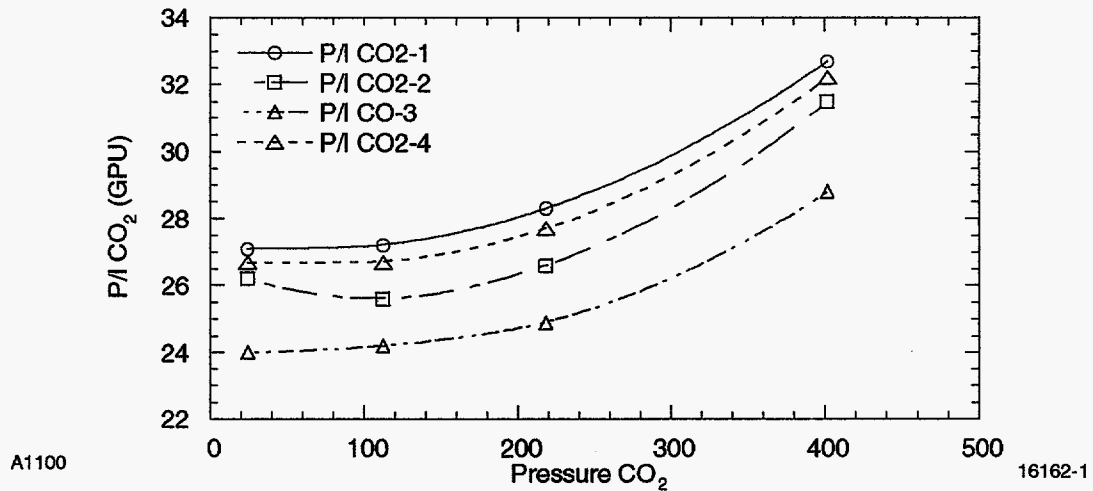


Figure 3-9 - CH₄ Permeance as a Function of CH₄ Pressure: MEM1 Membrane @ 23°C

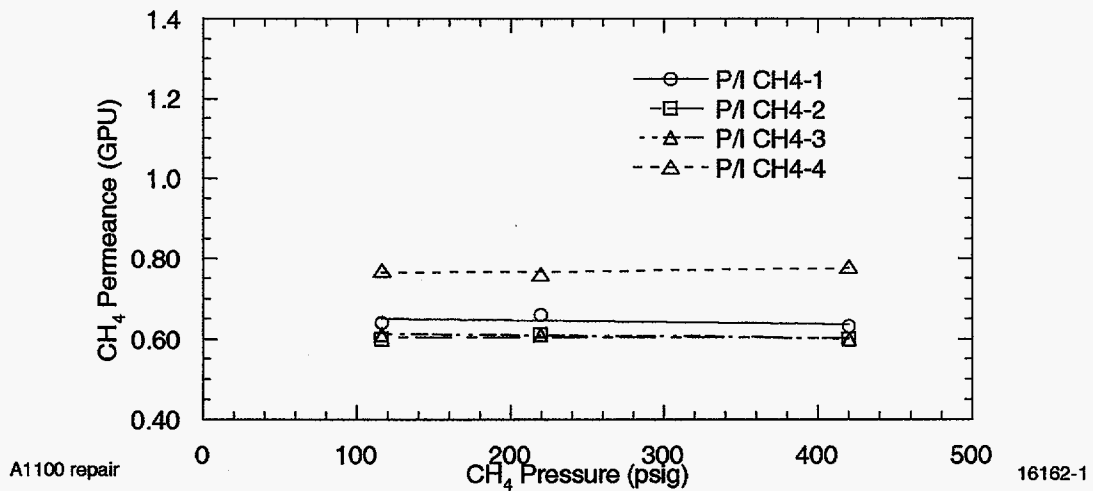
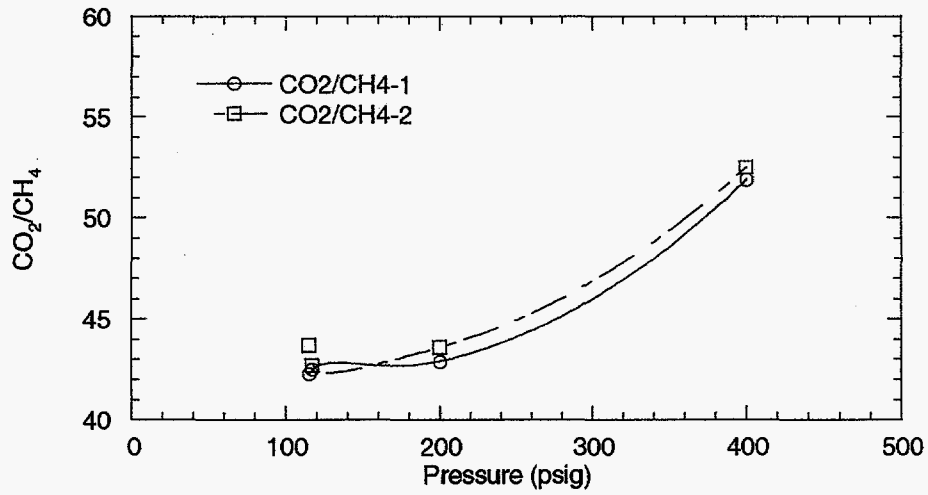
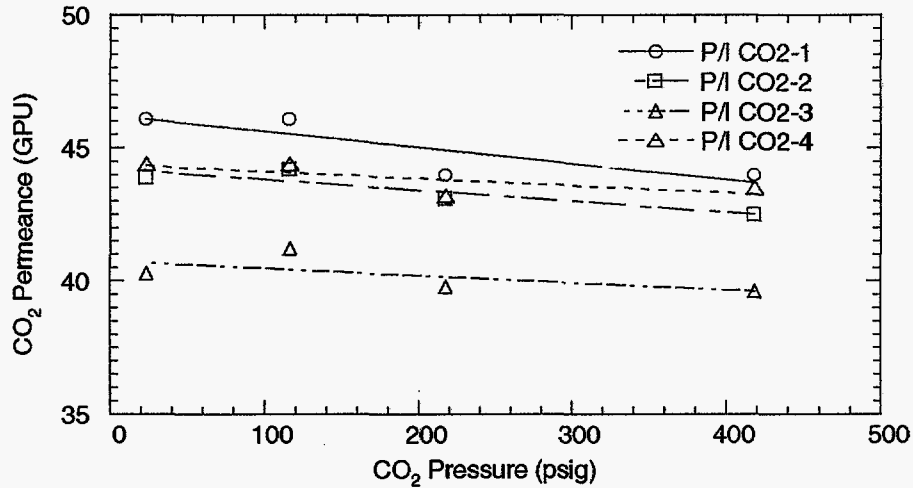


Figure 3-10 - Apparent Selectivity of MEM1 Membrane @ 23°C



The pure gas permselectivity of MEM1 test loops at 50°C is shown in Figures 3-11 and 3-12. At 50°C, the CO₂ permeance was independent of CO₂ pressure; i.e., no plasticization was occurring under these conditions. As expected, the CH₄ permeance was also independent of pressure, and the CO₂/CH₄ was stable.

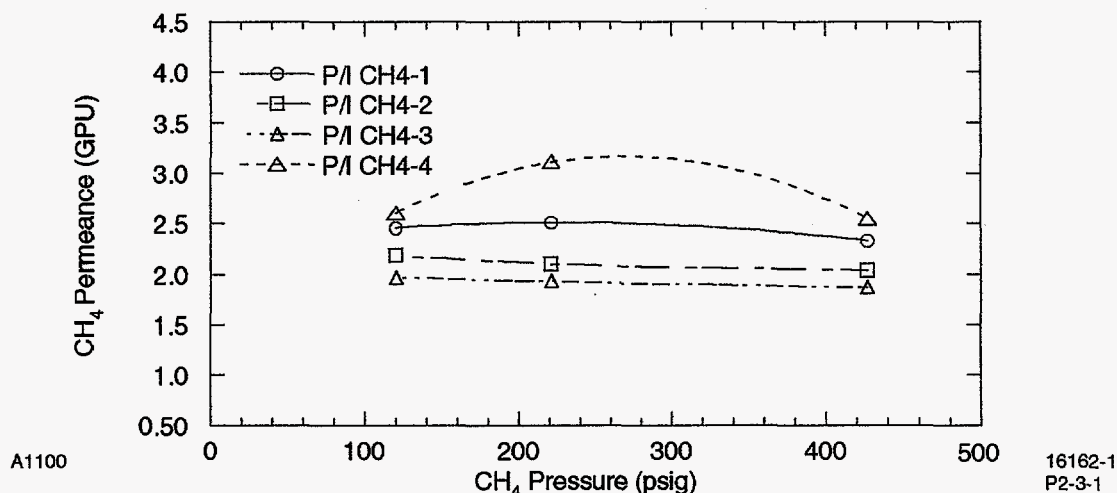
Figure 3-11 - CO₂ Permeance as a Function of CO₂ Pressure: MEM1 Membrane @ 50°C



A1100

16162-1
P2-3-2

Figure 3-12 - CH₄ Permeance as a Function of CH₄ Pressure: MEM1 Membrane @ 50°C



3.3 Mixed-Gas Testing of GDX and MEM1 Test Loops

Some preliminary evaluations of the mixed-gas permselectivity of GDX and MEM1 test loops were performed. In these tests the feed gas was a mixture of CO₂ and CH₄ (30/70) and was flowing through the shell side of the module under the conditions indicated in Table 3-2. The permeate composition and flow were determined at steady state, and the data were fed into an Aspen membrane module to calculate the membrane properties. The results indicate that no significant mixed-gas effects occur under these conditions.

Table 3-2 - Mixed Gas Test Summary: GDX and MEM1 @ 20°C

Ref. No.	Test Loop	Temp °C	Feed Press psig	Feed Rate cc/min	Perm Rate cc/min	Perm Composition		CO ₂ Recovery %	Membrane Properties	
						% CO ₂	% CH ₄		P/I CO ₂	CO ₂ /CH ₄
Feed Gas: 30.6 %CO ₂ 69.4 %CH ₄										
GDX005										
15727-30	PP062896-2-3	23	53	51.5	6.06	73.4	26.6	28.23	49.8	15.3
15727-40	"	23	52	26.1	5.16	67.5	32.5	43.61	41.4	12.1
15272-44	MR062796-4-4	23	53	51.3	5.75	79.6	20.4	29.16	65.4	28.6
15757-48	"	23	53	21.7	4.96	74.3	25.7	55.50	50.2	20.9
15727-50	"	23	74	52.1	8.26	78.2	21.8	40.52	51.5	20.1
MEM1										
15757-32	14529-82-15-6	23	52	51.7	2.28	88.4	11.6	12.74	23.2	52.6
15727-34	"	23	53	25.6	2.01	86.4	13.6	22.17	22.0	49.3
15727-58	"	60	50	52.9	4.35	82.9	17.1	22.28	46.9	36.0
15727-59	"	60	50	26.5	3.7	78.9	21.1	36.00	39.4	29.2
15727-60	"	60	75	52.3	6.92	82	18	35.46	38.4	25.5
15727-62	"	60	74	52.3	7.6	82.4	17.6	39.13	44.7	27.5
15727-63	"	60	74	103	8.5	85	15	22.92	46.6	29.4
15727-64	"	60	50	53.7	4.8	83.9	16.1	24.51	56.2	42.0
15727-65	"	60	50	53.4	4.75	83.8	16.2	24.36	53.6	39.9

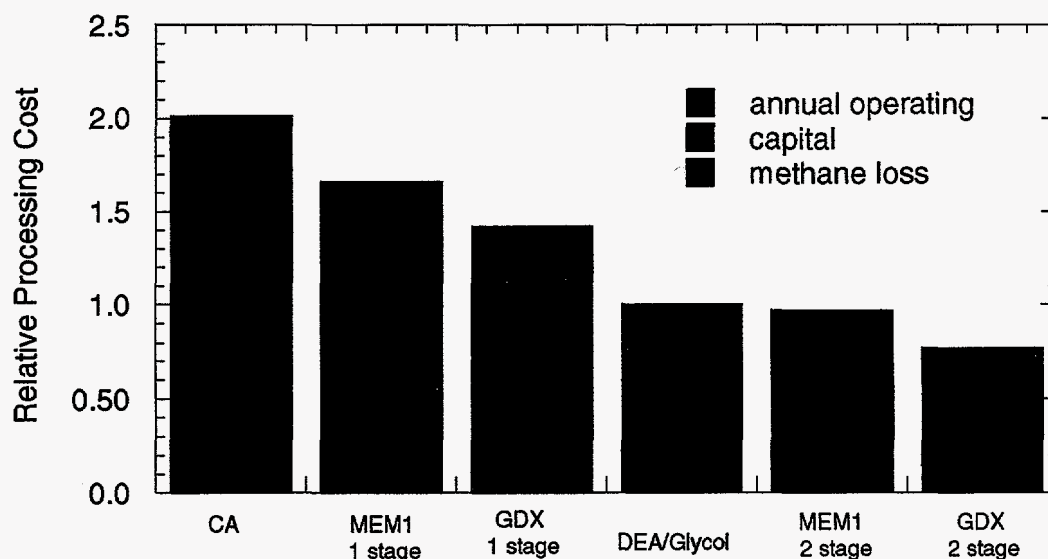
4.0 Membrane Engineering and Economic Analysis

Summary

An in-depth economic evaluation of the different techniques to remove CO₂ from natural gas was performed (see Figure 4-1). The purpose of this evaluation was to compare current technology economics to those for a new membrane polymer currently being explored under this Cooperative Agreement. Intrinsic permeation data was obtained on this new polymer as well as on benchmark membranes (MEM1 and MEM2). The data was used as input to an Aspen computer model to calculate the area requirements for both single and two-stage configurations as applied to our study case. The estimated membrane area was then used as inputs to a membrane-costing evaluation program to determine the overall gas processing costs (measured in \$/MSCF feed) associated with the technology. Economic and process performance data accumulated for other competing membrane technologies, as well as the primary non-membrane technology (amine scrubbers for CO₂ removal and glycol systems for dehydration), were also evaluated using the same base-case conditions. The conclusions from this study were that GDX provided the lowest processing cost alternative among the *single-stage* membrane systems presented, but the predominant technology of amine scrubbers (CO₂ removal) and glycol dehydrators still produced a 30% lower customer cost than the GDX membrane. This cost savings was primarily due to higher methane losses in the membrane systems. To lower these methane losses, a two-stage configuration of the same polymer was evaluated. A conventional two-stage design with permeate recompression was used with both MEM1 and GDX membrane modules to determine the processing costs. It was determined that both the MEM1 and GDX two-stage systems displayed more favorable economics than both single-stage designs or a scrubber/dehydrator. The two-stage GDX system provided the lowest overall processing costs. Sensitivities to flow rate and feed CO₂ content helped determine what operating conditions enhanced the advantages of the two-stage design.

Additionally, intangible membrane technology benefits not associated with economics (e.g., lack of moving parts, smaller space/weight requirements) must also be considered in assessing competitive technology.

Figure 4-1 - Evaluation of Several Different Techniques to Remove CO₂ from Natural Gas



4.1 Base Case Attributes

As a result of the market research efforts summarized in Chapter 2, the following base case was chosen for study:

- 35 MMSCFD feed gas at 125°F and 825 psia
- Feed gas composition: 87% CH₄, 7% CO₂, 5.74% N₂, 0.26% H₂O (saturated water vapor at 125°F)
- Product gas requirement: less than 2% CO₂ content, less than 4 lb H₂O/MMSCF

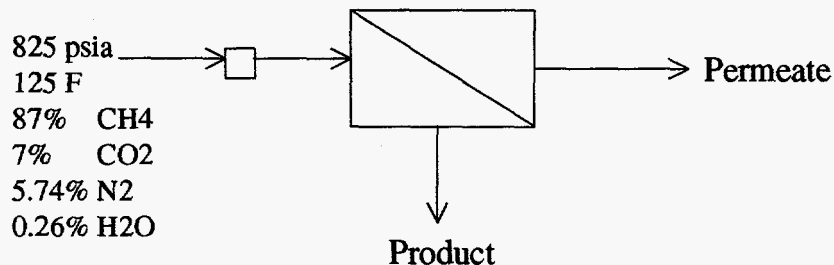
The nitrogen was a surrogate for all C₂ and higher hydrocarbons in the feed gas. The product gas requirements were obtained from typical pipeline specifications in the United States.

4.2 Single-Stage Processes

4.2.1 Basis

A generic single-stage membrane process is shown in Figure 4-2. The raw feed gas is heated and routed to the membrane. Carbon dioxide permeates the membrane, while the less permeable methane is enriched in the product stream.

Figure 4-2 - Generic Single-Stage Membrane Process



Of the polymers explored in the laboratory screening phase of this work, GDx was identified as having permselectivity superior to currently available cellulose acetate membranes. GDx polymer was spun into hollow-fiber membrane at pilot scale²¹ and underwent pure and mixed gas laboratory testing. The results from these tests were extrapolated to the base-case conditions and used as input for processing economics employing GDx in a single-stage configuration. The bases used in the calculations are summarized in Table 4-1.

Table 4-1 - Basis for Economic Figures for Membrane Technologies

1. Capital Payback

The total direct fixed capital (DFC) required to purchase and install the membrane assembly is assumed to be paid off on a monthly basis over a three-year period at a 7% interest rate.

2. Annual Operations

The annual operations costs are based on SRI International Report No. 190A, *Membrane Gas Separation Processes*, February 1990. Operations labor hourly costs have been escalated to 1996 dollars at 3% per year.

Annual operations costs consist of:

- Operations labor: 0.0625 personnel, \$27.09/hr rate
- Maintenance labor: 2%/yr of the DFC
- Control lab labor: 20% of operations labor
- Maintenance materials: 2%/yr of the DFC
- Operating supplies: 10% of operations labor
- Membrane replacement: 20% of membrane fiber replaced annually
- Plant overhead: 80% of total labor
- Insurance: 2%/yr of the DFC

3. Methane Loss

The amount of methane that exits through the permeate stream is multiplied by a fuel price of \$2.00/MMBTU (1123 BTU/SCF). An on-stream factor of 0.95 is assumed.

The ASPEN membrane model produced the two important parameters necessary to achieve product gas specifications: membrane area required and CH₄ loss to the permeate. The membrane area requirement was used in conjunction with Air Products' cost estimation program to determine the capital investment necessary by the gas processor. This information, combined with the methane losses, was used as input to an Excel program that calculates the gas processing costs. These costs were broken down into three sections:

- Capital payback
- Cost of annual operations

- Methane loss

4.2.2 GDX Membrane Optimization

A Taguchi statistical experiment design was set up to explore which design parameters have the greatest influence on methane loss and membrane area requirements. The Taguchi analysis of the module dimensions and membrane properties looked at five design variables for each membrane, for which the relative values are given in Table 4-2

Table 4-2 - Taguchi Analysis Variables and Values

<u>Variable</u>	<u>Units</u>	<u>Normalized Setpoints</u>		
		<u>#1</u>	<u>#2</u>	<u>#3</u>
Fiber Inner Diameter (ID)	Microns	1	1.67	2.33
Fiber Effective Length	Feet	1	2	
Presence of Sweep Gas (2% of Product)		Yes	No	
CO ₂ /CH ₄ Selectivity		1	2.5	
CO ₂ Permeability (MEM1 Membrane)	Relative GPU	1	2.5	
CO ₂ Permeability (GDX Membrane)	Relative GPU	3	7.5	

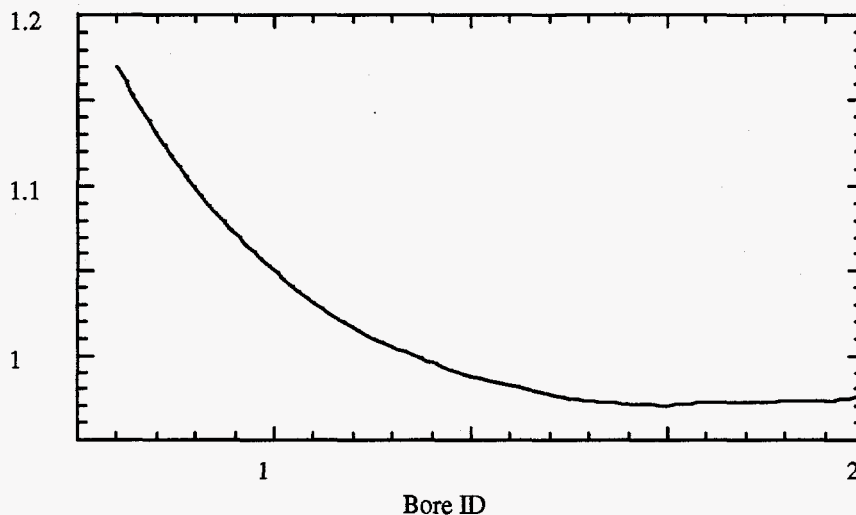
The response functions determined by the ASPEN membrane model were methane loss and area requirement to satisfy pipeline specifications for the base case. An orthogonal array of 64 ASPEN simulations was generated and used to determine the effect of the individual variables, as well as interactions between the variables on the response functions. It was determined that there are no significant variable interactions that affect either of the response functions.

1. The ASPEN membrane module inputs were modified to incorporate larger ID/OD combinations, and then processed using the base case to predict methane losses and area requirements.
2. The area requirements were placed in the membrane costing model to determine the number of modules necessary. As the ID/OD values were increased, the membrane area per module was decreased to maintain the same effective module diameter and packing efficiency as the original dimensions. This resulted in a larger number of modules to achieve a given membrane area requirement, and higher overall costs due to increased module components.
3. The membrane module requirements and methane losses were placed in the economic evaluation model to determine gas processing costs.

The Taguchi analysis yielded the following results:

- ◆ Increasing the fiber ID eliminates the effects of bore side pressure, minimizing methane loss.

Figure 4-3 - Processing Cost Sensitivity to Membrane Inner Diameter



◆ Once the fiber ID is optimized, (Figure 4-3) the overriding factor for methane loss is then simply the selectivity of the membrane fiber. As the selectivity is increased, the methane losses decrease. All other membrane design variables (fiber ID, fiber OD, and fiber length) have little effect in comparison.

As GDx membrane ID is increased, the savings due to reduced methane loss dominate the processing costs. However, at higher IDs, the bore side pressure drop is eliminated, and the loss in membrane area per module results in higher overall processing costs. The ID identified as the minimum processing cost has the economics provided in Table 4-3:

Table 4-3 - Optimized GDx Membrane Economic Evaluation Results (DEA=1)

Category	Relative Gas Processing Costs (/MSCF)
Capital Payback	0.1628
Annual Operations	0.1101
Methane Loss	1.1482
Total	1.4211

This represents approximately a 15% gas processing savings when compared to MEM1 membrane design economics (see below), and the methane losses (8.4% of feed gas) are slightly less than MEM1. This represents essentially the lowest methane losses possible for a membrane fiber of this selectivity in a single-stage design.

Competing Membrane Technologies

Information sufficient for an economic evaluation has been gathered on two competing membrane technologies (MEM1 and MEM2) and a cellulose acetate spiral-wound membrane. The economic results of these two technologies will be compared against the GDx case previously discussed.

4.2.3 MEM1 Membrane

Benchmarking studies were performed against MEM1, a ‘production’ membrane not used in natural gas applications. With the MEM1 membrane design, the ASPEN membrane model produced the two important parameters necessary to achieve product gas specifications: membrane area required and CH₄ losses to the permeate. The membrane area requirement was used in conjunction with a membrane cost estimation program to determine the capital investment necessary by the gas processor. This information, combined with the methane losses, was input to an Excel program that calculated the gas processing costs. Again, these costs were broken down into three sections:

- Capital payback
- Cost of annual operations
- Methane loss

The results are provided in Table 4-4:

Table 4-4 - MEM1 Economic Evaluation Results (DEA=1)

Category	Relative Gas Processing Costs (/MSCF)
Capital Payback	0.2649
Annual Operations	0.1687
Methane Loss	1.2260
Total	1.6596

Greater than 70% of the costs are due to methane losses because 9.0% of the feed CH₄ exits the permeate and is assumed to be unrecoverable.

The intrinsic variables and module design information for MEM2 were evaluated using the same base case and economic parameters employed above. ASPEN simulations using countercurrent and cocurrent flow patterns were executed, and the results interpolated to predict performance based on 50% cross-flow/50% countercurrent-flow information. The membrane costing model was used along with the membrane area/module information provided.

For the cellulose acetate spiral wound membrane, intrinsic variables were obtained from the GRI Topical Report entitled *Development of a Database for Advanced Processes to Remove Carbon Dioxide from Subquality Natural Gas* (GRI-93/0247). The area requirements for the base case were multiplied by \$10/square foot to arrive at the DFC value. The rest of the economic model is identical to the previous membrane analyses.

Results for the two competing membrane technologies are provided in Table 4-5:

Table 4-5 - Competing Technologies Economic Evaluation Results

Category	Relative Gas Processing Costs (/MSCF)	
	MEM2	Cellulose Acetate Spiral Wound
Capital Payback	0.0741	0.0939
Annual Operations	0.0565	0.0880
Methane Loss	1.4923	1.8232
Total	1.6236	2.0059

MEM2 hollow-fiber overall economic results are similar to the MEM1 membrane results (15% higher than the optimized GDX membrane results), while the cellulose acetate results are significantly higher due to methane losses from low selectivity.

4.2.4 Amine Scrubber/Glycol Dehydrator

The most prevalent technologies currently being used for natural gas CO₂ and H₂O removal are amine scrubbers and glycol dehydrators, respectively. Economic data for this process were obtained from the GRI Topical Report entitled *Business Characteristics of the Natural Gas Conditioning Industry* (GRI-93/0342) and applied to the same base case used for the membrane technologies. The scrubber evaluated used diethanol amine (30 weight percent solution), with flow of 0.26 gal solution circulated per SCF gas feed. The dehydrator circulated 3 gallons of glycol per lb water removed. The economic results are provided in Table 4-6:

Table 4-6. DEA Scrubber/Glycol Dehydrator Relative Economic Evaluation Results

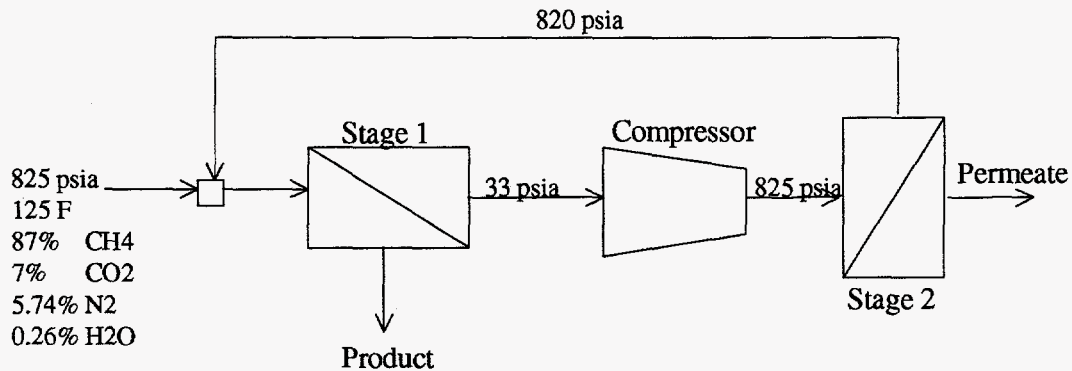
Category	Relative Gas Processing Costs (/MSCF)
Capital Payback	0.3749
Annual Operations	0.4035
Methane Loss	0.2216
Total	1.000

Significantly lower methane losses (approximately 1.7% of feed) more than compensate for higher capital and annual costs to produce a final gas processing cost lower than any of the membrane technologies discussed thus far. In addition, it should be noted that this analysis assumed new scrubber/dehydrator equipment. There is a significant market of used scrubber/dehydrator equipment at reduced prices, and the GRI report states that 20% of the plants responding to a survey have some used gas processing equipment.

4.3 Two-Stage Designs

Figure 4-4 provides a diagram of the two-stage system to be considered. The permeate from the first stage is recompressed and directed to a smaller second stage, where the retentate is recycled and mixed with the feed gas. Economic optimization performed on both membrane materials described below indicates that an Area 1:Area 2 ratio of approximately 9:1 produces the lowest overall gas processing cost, and will be used in all process simulations. A four-stage centrifugal compressor was used to raise first-stage permeate pressure from 33 to 825 psia. In a technique similar to the single-stage study, ASPEN simulations of the two-stage system were used to determine the parameters of importance for processing cost (membrane area requirements, methane loss, compressor requirements). These values were then employed in a membrane costing evaluation program. The economic bases were the same as those used for the single-stage cases.

Figure 4-4 - Generic Two-Stage Membrane System with Interstage Compression



4.3.1 Two-Stage GDX Membrane

With the same membrane fiber geometry and module characteristics as MEM1, the economic evaluation on the two-stage GDX system reveals the following (Table 4-7):

Table 4-7 - Two-Stage GDX Membrane Relative Economic Evaluation Results (DEA=1)

Category	Relative Gas Processing Costs (/MSCF)
Capital Payback	0.3742
Annual Operations	0.2480
Methane Loss	0.1445
Total	0.7667

This represents a 23% reduction in processing cost from the scrubber/dehydrator option.

4.3.2 Two-Stage MEM1 System

The membrane costing evaluation program results for a two-stage MEM1 system are displayed in Table 4-8, along with the amine scrubber/glycol dehydrator processing costs from the earlier work:

Table 4-8 - Two-Stage MEM1 Membrane Relative Economic Evaluation Results (DEA=1)

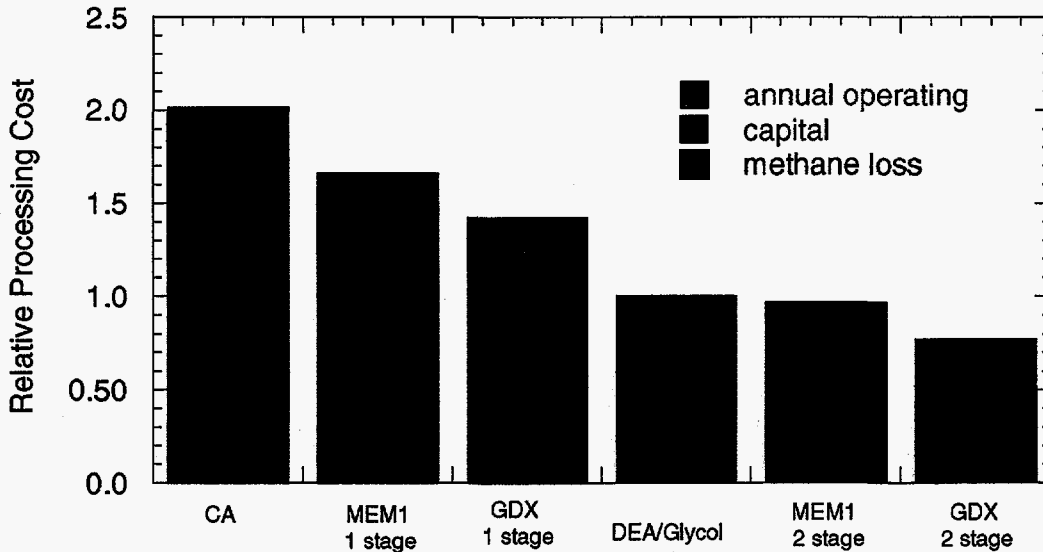
Category	Relative Gas Processing Costs (/MSCF)	
	Two Stage MEM1 System	DEA Scrubber/Glycol Dehydrator
Capital Payback	0.5121	0.3749
Annual Operations	0.3294	0.4035
Methane Loss	0.1247	0.2216
Total	0.9662	1.0000

This shows that the two-stage MEM1 system has a slightly lower overall cost than the scrubber/dehydrator technology, and is significantly lower in operating cost than a MEM1 single-stage system.

The reason for overall cost reduction in both GDx and MEM1 is the lower methane losses associated with the two-stage design. In the single-stage MEM1 evaluation, 9% of the feed methane was lost to the permeate, and methane losses accounted for over 70% of the processing cost. In the two-stage evaluation, less than 1% of the feed methane was lost, and methane losses accounted for 14% of the processing cost. Capital and operating costs, in turn, increased in comparison to single-stage membrane products due to the addition of the compressor. However, the savings due to reduced methane losses more than offset the increased capital costs, making the two-stage system an economically favorable alternative over the single-stage system.

Figure 4-5 graphically compares the relative processing costs for single- and two-stage GDx and MEM1, along with the conventional amine/dehydrator. The figure shows that a two-stage GDx system represents the lowest customer cost of all the natural gas processing technologies evaluated using the base-case conditions.

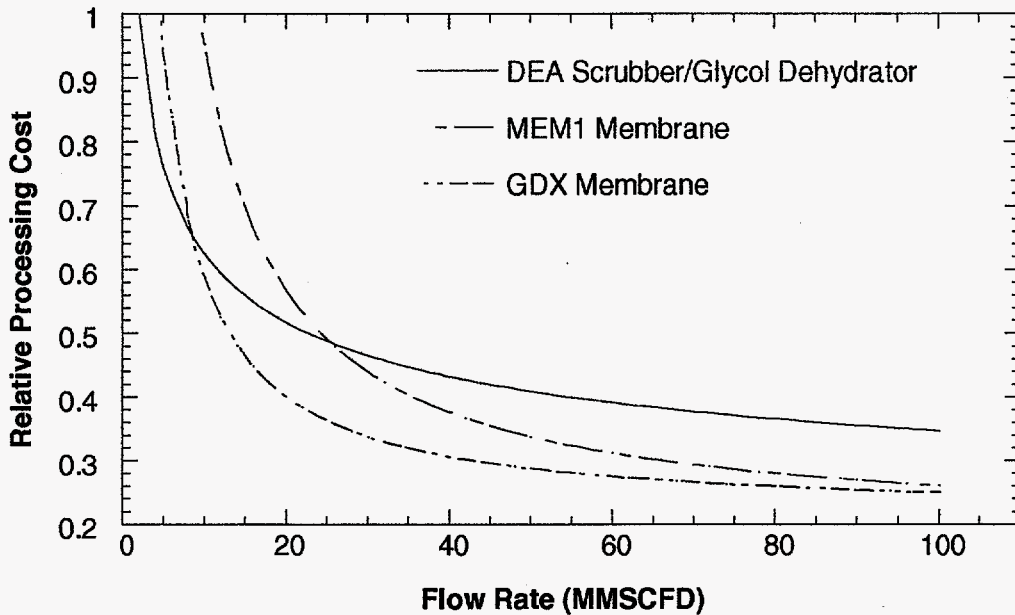
Figure 4-5 - Technology Comparison



4.4 Sensitivity to Process Variables

To explore possible gas processing situations other than the base case, the sensitivity of the processing cost to two key variables (daily production rate and feed gas CO₂ content) was performed. The results for production rate (the base case value is 35 MMSCFD) are given in Figure 4-6:

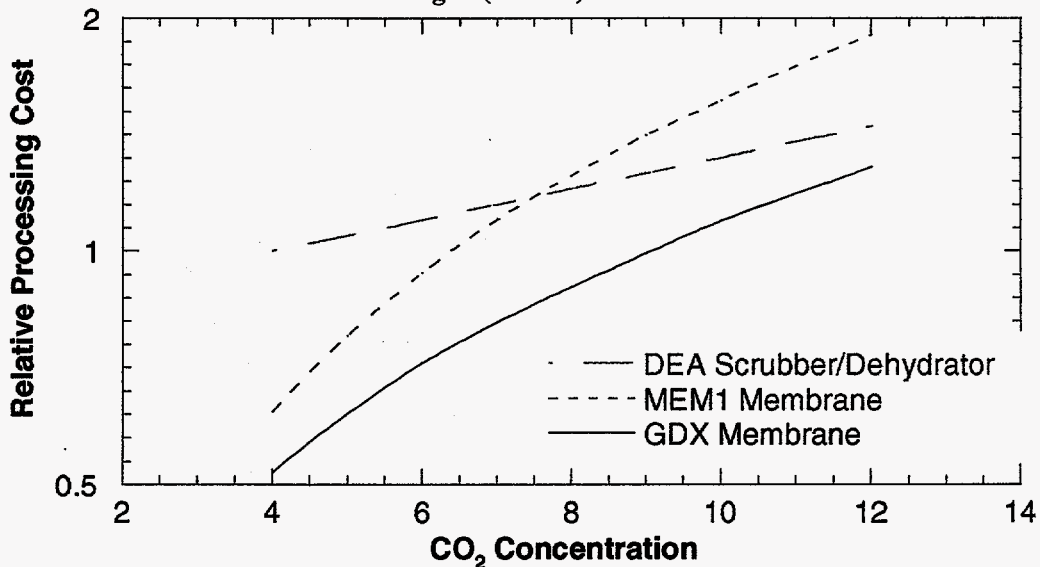
Figure 4-6 - Economics vs Flow Rate for Two-Stage Membrane and Scrubber/Dehydrator Technologies (DEA=1)



At low production rates (<20 MMSCFD), the two-stage MEM1 design represents the highest processing cost alternative. At higher flow rates, however, the two-stage MEM1 membrane approaches the processing costs of the two-stage GDX membrane, while achieving savings over the scrubber/dehydrator technology.

Another important natural gas processing variable is the CO₂ content in the feed gas. Results from sensitivity studies are summarized in Figure 4-7.

Figure 4-7 - Economics vs Feed Rate CO₂ Content for Two-Stage Membrane and Scrubber/Dehydrator Technologies (DEA=1)



The economic advantage for two-stage membrane technology is greatest in the low CO₂ content region, with the two-stage MEM1 system processing cost the highest of all technologies in the high CO₂ content region.

5.0 Recommendations for Further Work

As a result of work performed during this reporting period, Air Products recommends the following tasks to complete this program and demonstrate viable advanced membrane technology. Each task is described in detail in the Statement of Work for this Cooperative Agreement.

- Initiate laboratory challenge testing on small modules to examine the effects of wellhead gas contaminants on membrane performance (e.g., water vapor, low-level hydrocarbons, low-level hydrogen sulfide).
- Initiate field testing of MEM1, GDx and subsequent new polymers achieving preliminary targets as set forth in this report. To ensure maximum utility of the field test data, testing will be conducted on the largest size modules that can be reasonably fabricated under this agreement. The goal is to evaluate full-size commercial units and confirm laboratory properties.
- Continue development of next-generation polymer membrane materials as per the Statement of Work for this Cooperative Agreement.

Successful performance of these tasks will lead to a decision on a commercially viable membrane system and result in the completion of this program.

6.0 Acknowledgments

The following people made outstanding contributions to this program and deserve a wealth of thanks: Joseph R. Gogatz for membrane module fabrication and evaluation; John Dewhurst for help with the Taguchi design and analysis; Ken Jones, Bill Pope, Wayne Bollinger and Charles Page for their input and feedback on the economic analysis; Marianne Phillips for editing this manuscript; and lastly to Brian M. O'Neil, Douglas Hooker and Ehr-Ping HuangFu for their diligence and efficiency and administration of this cooperative agreement

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