Nitrogen Removal from Natural Gas

Topical Report

September 29, 1995- September 30, 1996

Work Performed Under Contract No.: DE-AC21-95MC32199

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Membrane Technology and Research, Inc.
1360 Willow Road, Suite 103
Menlo Park, California 94025

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government, Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SUMMARY

According to a 1991 Energy Information Administration estimate, U.S. reserves of natural gas are about 165 trillion cubic feet (TCF). To meet the long-term demand for natural gas, new gas fields from these reserves will have to be developed. Gas Research Institute studies reveal that 14% (or about 19 TCF) of known reserves in the United States are **subquality** due to high nitrogen content. Nitrogen-contaminated natural gas has a low Btu value and must be upgraded by removing the nitrogen.

In response to the problem, the Department of Energy is seeking innovative, efficient nitrogen-removal methods. Membrane processes have been considered for natural gas **denitrogenation**. The challenge, not yet overcome, is to develop membranes with the required nitrogen/methane separation characteristics. Our calculations show that a methane-permeable membrane with a **methane/nitrogen** selectivity of 4 to 6 would make denitrogenation by a membrane process viable.

The objective of Phase I of this project was to show that membranes with this target selectivity can be developed, and that the economics of the process based on these membranes would be competitive. Gas permeation measurements with membranes prepared from two rubbery polymers and a superglassy polymer showed that two of these materials had the target selectivity of 4 to 6 when operated at temperatures below -20 oC. An economic analysis showed that a process based on these membranes is competitive with other technologies for small streams containing less than 10% nitrogen. Hybrid designs combining membranes with other technologies are suitable for higher-flow, higher-nitrogen-content streams.

This Phase I work demonstrated clearly that natural gas denitrogenation using **methane-permeable** membranes is technically and economically feasible. Further work in Phase II will show which of the two candidate membranes is the most suitable for scale-up to membrane modules for laboratory tests followed by tests of the process in the field. This report includes a bench-scale test plan for the modules.

TABLE OF CONTENTS

SUMMARY	i
1. INTRODUCTION	1
1.1 Significance of the Problem	1
1.2 Technical Approach	3
1.3 Key Issues	7
2. PHASE I OBJECTIVES	9
3. EXPERIMENTAL TECHNIQUES AND PROCEDURES	10
3.1 Membrane/Film Preparation... ..	10
3.2 Membrane Permeation Test System	11
3.3 Experimental Protocol	12
4. EXPERIMENTAL RESULTS	12
4.1 Summary of Phase I Results	12
4.2 Selection of Polymers	13
4.3 Silicone Rubber Membrane	14
4.4 Pebax 2533 Membrane	15
4.5 PTMSP Films	17
4.6 Laboratory-Scale Module Tests... ..	22
5. ECONOMIC ANALYSIS	22
5.1 Economic Analysis of Membrane Denitrogenation Applications	23
5.2 Competing Technologies	30
5.3 Hybrid Designs	31
5.4 Size of Denitrogenation Application	34
6. BENCH-SCALE TEST PLAN	36
7. CONCLUSIONS	39
REFERENCES	41

LIST OF FIGURES

Figure 1.	Simplified block diagram of a low-temperature membrane process for natural gas denitrogenation coupled with higher hydrocarbon liquid recovery	4
Figure 2.	Simple one-stage separations of 10% nitrogen/90% methane feed gas to produce 50% nitrogen/50% methane reject stream and a 4% nitrogen/96% methane product gas	7
Figure 3.	Schematic diagram of an MTR composite membrane	10
Figure 4.	Flow diagram of low-temperature membrane testing system	11
Figure 5,	Methane/nitrogen selectivity as a function of feed temperature for the PTMSP membrane	13
Figure 6.	Effect of feed temperature on the pressure-normalized flux of propane, methane and nitrogen in silicone rubber at a feed pressure of 400 psia	14
Figure 7.	Effect of feed temperature on the propane/nitrogen, propane/methane, and methane/nitrogen selectivity in silicone rubber	15
Figure 8.	Effect of feed temperature on the pressure-normalized flux of propane, methane and nitrogen in Pebax 2533 at a feed pressure of 200 psia	16
Figure 9.	Effect of feed temperature on the methane/nitrogen, propane/methane and propane/nitrogen selectivity in Pebax 2533	17
Figure 10.	Effect of feed temperature on the permeation flux of propane, methane and nitrogen in PTMSP at a feed pressure of 200 psia	18
Figure 11.	Effect of feed temperature on the methane/nitrogen and propane/nitrogen selectivity of a PTMSP film	18
Figure 12.	Effect of the fractional saturation of propane in the feed gas on the permeation flux of propane, methane and nitrogen in PTMSP	20
Figure 13.	Effect of the fractional saturation of propane in the feed on the propane/nitrogen and methane/nitrogen selectivity in PTMSP	20
Figure 14.	Permeability of PTMSP membranes with a hydrogen/butane mixture and with pure hydrogen in a prolonged test....	21

LIST OF FIGURES - (continued)

Figure 15.	Single-stage membrane process utilizing available gas pressure to perform cooling and compression work for the separation of nitrogen from methane and for the recovery of natural gas liquids	23
Figure 16.	Effect of permeate pressure on (a) the capital cost and (b) the processing cost of the membrane system for the separation of nitrogen from natural gas	26
Figure 17.	Two-stage membrane process for treating low-flow (2-20 MMscfd) high-nitrogen-content (>10%) natural gas	27
Figure 18.	Single-stage membrane process for denitrogenation of natural gas to upgrade heating value and recover natural gas liquids	28
Figure 19.	Hybrid process combining a single-stage membrane system with an adsorption process for treating low-flow, high-nitrogen-content natural gas	32
Figure 20.	Hybrid membrane/adsorption process for treating high-flow, low-nitrogen-content natural gas streams	33
Figure 21.	Hybrid membrane/cryogenic distillation process for treating high-flow, high-nitrogen-content natural gas.. . . .	34
Figure 22.	Reserves volume as a function of nitrogen concentration in natural gas	35
Figure 23.	Flow diagram of the existing bench-scale test apparatus for determining the performance of membrane modules.. . . .	36
Figure 24.	Flow diagram, showing pressure (P), temperature (T), and flow (F) monitoring points, of the field test skid for the evaluation of 3-inch and 8-inch modules for the removal of nitrogen from natural gas	39

LIST OF TABLES

Table 1.	Processes Currently Used or Under Development for Removal of Nitrogen from Natural Gas	2
Table 2.	Intrinsic Permeability Properties of Polymers (from pure-gas measurements)	6
Table 3.	Summary of Permeability and Selectivity of the Three Membranes Tested in Phase I	12
Table 4.	Membrane Materials Chosen for Feasibility Study for Denitrogenation of Natural Gas	14
Table 5.	Gas Composition and Membrane Permeation Properties for Base-Case Economic Calculations	23
Table 6.	Capital and Operating Costs of a 5-MMscfd Membrane Nitrogen-Removal Plant .	25
Table 7.	Capital and Operating Costs for Denitrogenation of Low Btu Natural Gas for Upgrade to Pipeline Specification of 1,000 Btu/scf	29
Table 8.	Cost Comparison for Various Technologies Currently Available for Removal of Nitrogen from Subquality Natural Gas	31
Table 9.	Distribution of Non-Associated Gas with 4% or More Nitrogen in 1988 Reserves .	36
Table IO.	Parameters for Phase II Bench-Scale Module Test Program	37

1. INTRODUCTION

1.1 Significance of the Problem

According to a 1991 Energy Information Administration estimate, U.S. reserves of natural gas are about 165 trillion cubic feet (TCF). To meet the long-term demand for natural gas, new gas fields from these reserves will have to be developed. This has several important consequences.

First, low-quality fields will have to be tapped, increasing the proportion of low-quality gas in the gas supply and hence the extent of treatment required to bring the gas to pipeline specifications,¹ These factors highlight the need for less expensive treatment technology. Second, much of today's gas production is from large, accessible fields, whereas new production will be increasingly from small, remote or offshore fields. As a result, the need for technology suitable to treat small gas streams will increase. Third, studies performed by the Gas Research Institute (GRI Executive Summary, March, 1993)² reveal that 14% (or about 19 TCF) of known reserves in the United States are subquality due to high nitrogen content. Nitrogen-contaminated natural gas has a low Btu value and has to be upgraded by removing the nitrogen. In many cases, such reserves cannot be exploited because of the lack of suitable nitrogen-removal technology. Processes applicable to small-scale plants are particularly needed. For large scale plants, cheaper, more reliable technologies are required.

In response to the problem, the Department of Energy is seeking innovative, efficient nitrogen-removal methods. Table 1 summarizes the principal processes in use or under development: cryogenics, pressure swing adsorption (PSA), lean oil adsorption, and nitrogen adsorption.

Table 1. Processes Currently Used or Under Development for Removal of Nitrogen from Natural Gas

Process (Status)	Method of Separation	Application	Comments
Cryogenic Distillation (Proven commercially)	Condensation and distillation at cryogenic temperatures	High flow rate applications	High methane recovery Significant pretreatment cost High capital costs Reliability a problem
Pressure Swing Adsorption (PSA) (Limited commercial success)	Adsorption of methane	Generally small to medium flow rates	Pretreatment required High capital costs High operating costs Moderate methane recovery
Lean Oil Absorption (New process)	Absorption of methane in chilled hydrocarbon oil	Suitable for high nitrogen content stream	High capital costs Processing costs significant Need to absorb bulk of methane increases equipment size
Nitrogen Absorption (Research stage)	Selective absorption of nitrogen in chelating solvent		No methane recompression needed Stability of chelating compound suspect

Of the processes shown in Table 1, cryogenic processes are the only technology used on any scale. Costs for cryogenic processes vary with stream composition, but are in the range \$0.30-0.50/Mscf for plants handling 75 MMscfd and increase to more than \$1.00/Mscf for plants handling 2 MMscfd or less. The other processes are more expensive and have not yet found industry acceptance.

Membrane processes have also been considered for natural gas denitrogenation. The challenge, not yet overcome, is to develop membranes with the required nitrogen/methane separation characteristics. Either glassy polymers, which are usually nitrogen-permeable, or rubbery polymers, which are usually methane-permeable, could be used. Obtaining suitable nitrogen-permeable membranes does not seem feasible. Our calculations show that a nitrogen/methane selectivity of at least 15 is required to make this type of membrane economically viable; the highest selectivity available with current polymers is only about 2-3. Ceramic membranes exhibiting significantly higher nitrogen/methane selectivities have recently been reported in the literature.³ Membrane permeation tests have been performed using very small membrane disks. Results indicate that at high temperatures ($> 200^{\circ}\text{C}$) the membranes exhibit very high nitrogen/methane selectivities at modest nitrogen permeation fluxes for experiments performed with pure gases. The effects of other components of natural gas on the membrane properties and effects of these at the higher temperatures have not been reported. Also, compared to conventional polymer membranes, it is notoriously difficult to make modules from ceramic membranes, as would be required for commercial separations.

On the other hand, for a methane-permeable membrane to be viable, a methane/nitrogen selectivity of 4 to 6 would suffice. The objective of this Phase I project was to determine whether this target membrane selectivity can be achieved, and, if so, whether a process based on such a membrane will be technically and economically viable.

1.2 Technical Approach

Our approach to denitrogenation of **subquality** natural gas to pipeline specifications is to use methane-permeable membranes in the innovative process design shown in Figure 1. All components of the process except the membrane are completely developed and commercially available. By integrating membrane separation with a turbine **expander/compressor** the energy used in the membrane cooling process is minimized, and most of the high-value C_{3+} hydrocarbons (NGL) are recovered.

The three main features of the process are:

- Use of high-performance methane-permeable membranes at low temperatures to separate the feed gas stream into a methane-rich product stream, and a nitrogen-rich waste gas stream.
- Expansion of the waste nitrogen stream in a turbo-expander/compressor assembly to cool the feed gas, while providing some of the work of compression for the purified methane stream from the membrane system.
- Recovery of the valuable C_{3+} higher hydrocarbons (natural gas liquids) from the high-pressure feed stream by condensation, using the cooling provided by the chilled waste gas.

Figure 1. Simplified block diagram of a low-temperature membrane process for natural gas denitrogenation coupled with higher hydrocarbon liquid recovery.

The low-pressure nitrogen-rich gas will provide the fuel required to power the gas engine, while the condensed natural gas liquids and the high-pressure natural gas will be the revenue-producing products. More complex designs, involving integration of the membrane system with cryogenic or PSA systems, would be used for larger streams from which maximum methane recovery is desirable.

The process illustrated in Figure 1 requires methane-permeable membranes with a methane/nitrogen selectivity of 4 to 6, depending on the concentration of the nitrogen in the feed gas. The Phase I work demonstrated the feasibility of achieving such selectivities at temperatures of -20 to -50 °C. A brief discussion of the factors that determine membrane selectivity follows.

A synthetic polymer membrane separates the components of a gas or vapor mixture because the components permeate the membrane at different rates. The permeability, P [$\text{cm}^3(\text{STP}) \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$], of a polymer membrane material for a gas is defined as the rate at which that gas moves through a standard thickness (1 cm) of the material under a standard driving force (a pressure difference of 1 cmHg). A measure of the ability of a membrane to separate two gases is the selectivity, α , defined as the ratio of the gas permeabilities, P_1/P_2 . Selectivity can also be expressed as^{4,5}:

$$\alpha = \frac{D_1}{D_2} \cdot \frac{k_1}{k_2} \quad (1)$$

where D is the diffusion coefficient of the gas in the membrane [cm^2/s], which is a measure of the gas mobility, and k is the Henry's law sorption coefficient, which links the concentration of the gas in the membrane material to the pressure in the adjacent gas [$\text{cm}^3(\text{STP})/\text{cm}^3\cdot\text{cmHg}$]. The *intrinsic* selectivity of a polymer material is established by measuring the permeabilities with pure gas or vapor samples, then calculating the ratio. The *actual* selectivity obtained in a real separation process is established by making permeation measurements with gas mixtures.

In glassy polymers, the dominant feature in the selectivity is the ratio of the diffusion coefficients, D_1/D_2 , which is heavily dependent on the ratio of the molecular sizes. In rubbery materials, the dominant feature is the ratio of the sorption coefficients, k_1/k_2 , which reflects the ratio of the condensabilities of the two permeants. Methane is a larger molecule than nitrogen, but is also slightly more condensable. Because the effects of condensability and molecular size are opposed, membranes ranging from slightly nitrogen-selective (diffusion coefficient controlled) to moderately methane-selective (volubility or condensability controlled) can be produced.

Table 2 shows the intrinsic permeabilities of a number of polymers to nitrogen and methane, ranked in order of decreasing nitrogen/methane selectivity. The data were obtained at MTR or taken from the literature. Stern et al. studied the gas permeabilities of specialty silicone polymers.⁶ Of these, the two polymers listed in Table 2, poly(siloxylene-siloxane), and poly(p-silphenylene-siloxane), have the highest methane/nitrogen selectivity. The polyimide data are taken from recent papers by groups at the University of Texas at Austin^{7,8} and at Yamaguchi University.⁹ Only the most nitrogen-permeable polyamides from these studies are listed.

Table 2. Intrinsic Permeability Properties of Polymers (from pure-gas measurements).

Polymer	Permeability (10^{-10} cm ³ (STP)·cm/ cm ² ·s·mmHg)		Selectivity (-)	
	N ₂	CH ₄	N ₂ /CH ₄	CH ₄ /N ₂
Polyimide (6FDA-mp' ODA)	0.26	0.13	2.1	0.5
Polyimide (6FDA-BAHF)	3.10	1.34	2.3	0.4
Polyimide (6FDA-IPDA)	1.34	0.70	1.9	0.5
Polyimide (PMDA-MDA)	0.20	0.01	2.0	0.5
Cellulose acetate	0.35	0.43	0.8	1.2
Polycarbonate	0.37	0.45	0.8	1.2
Polysulfone	0.14	0.23	0.60	1.7
Polydimethylsiloxane-dimethylstyrene	103	335	0.30	3.3
Polydimethylsiloxane (silicone rubber)	230	760	0.30	3.3
Poly(siloxylene-siloxane)	91	360	0.25	4.0
Poly(p-silphenylene-siloxane)	3	12	0.25	4.0
Polyamide-polyether copolymer	4.8	20	0.24	4.2

As shown in Table 2, polymers can be either methane-selective or nitrogen-selective; a membrane with a high selectivity of either kind could be applied to denitrogenation of natural gas. However, **nitrogen-permeable** polymers have practical disadvantages. Such-polymers are generally very impermeable and so insoluble that preparation of high-flux membranes is difficult. More importantly, the most selective nitrogen-permeable membrane only has a selectivity of 2-3. This means that, as well as permeating nitrogen, the membrane would also permeate a large amount of methane, reducing process efficiency.

Figure 2 shows trial calculations performed with a methane-permeable and a **nitrogen-permeable** membrane. The membrane selectivity required to separate a gas containing 10% nitrogen and 90% methane into two streams, one containing 4% nitrogen to be delivered to the pipeline and the other containing 50% nitrogen to be used as onsite fuel, has been calculated. The separation corresponds to 93% recovery of methane in the product gas stream, a very acceptable target for a denitrogenation process. A methane-permeable membrane with a **methane/nitrogen** selectivity of 6 is able to achieve the target separation, Table 2 shows that several known membranes have close to this selectivity. On the other hand, a nitrogen-permeable membrane must have a methane/nitrogen selectivity of 17 to achieve the target separation. The best nitrogen-selective membrane in Table 2 has a selectivity of 2.3, very far from the value required. This project, therefore, focuses on developing methane-selective membranes. Although this means the permeate gas must be recompressed, this cost is not enough to significantly impact process economics, especially if the permeate pressure is optimized for the system.

Figure 2. Simple one-stage separations of 10% nitrogen/90% methane feed gas to produce 50% nitrogen/50% methane reject stream and a 4% nitrogen/96% methane product gas. This target separation can be achieved by a methane-permeable membrane (a) having a selectivity of 6, close to today's membranes. The target separation requires a **nitrogen**-permeable membrane (b) to have a selectivity of 17, which is far above that of the best membranes known.

1.3 Key Issues

The principal technical issue to be addressed and the focus of the Phase I work was to determine whether adequate methane/nitrogen membrane selectivity can be achieved. Two types of polymer material—rubbery and superglassy—appeared to have the potential of achieving this selectivity at low temperatures.

Rubbery polymers are likely candidates because of the different way in which temperature affects the diffusion and sorption coefficient terms in equation (1). Diffusion coefficients decrease with decreasing temperature; sorption coefficients increase. Therefore, for permanent gases such as nitrogen, for which the diffusion coefficient dominates, the permeability is expected to decrease with decreasing temperature. For organic vapors, for which the sorption coefficient dominates, the permeability is expected to increase with increasing temperature. Because temperature affects the **permeabilities** of vapors and gases oppositely, selectivity should increase as temperature decreases. This effect is quite large for the heavier hydrocarbons found in natural gas, C₄ and above, but our data on methane were limited. We expected a modest increase in methane/nitrogen selectivity from 2-4 to >5 on cooling from 25°C to -40°C for rubbery polymers such as silicone rubber, poly(siloxylene-siloxane), and polyamide-polyether copolymers.

Superglassy polymers, such as PTMSP, were considered for different reasons. Operation of most glassy polymers at lower temperature would result in significantly reduced permeation due to decreased diffusivity at lower temperature and generally lower selectivity. However, the unusually high free volume of superglassy polymers provides exceptional permeation properties. PTMSP was discovered by researchers in Japan a few years ago.¹⁰ Gas permeabilities in PTMSP are orders of magnitude higher than those of conventional glassy polymers, and are even substantially higher than those of silicone rubber, the most permeable rubbery polymer known.⁴ The extremely high free volume of PTMSP provides a sorption capacity as much as 10 times greater than that of conventional glasses. More dramatically, the penetrant diffusivities are 103-106 times greater than the corresponding diffusivities in conventional glassy polymers. This combination of high gas solubilities and extremely high diffusivities gives extraordinarily high permeabilities.^{4,10}

For permanent gas mixtures, the high permeabilities are coupled with low selectivities and, to date, PTMSP has not been of practical value for any industrial separation application. Recent studies by Auvil et al.,¹¹ and at MTR, however, indicate that the permeabilities of permanent gases in PTMSP are dramatically reduced by the co-permeation of a large, condensable penetrant such as carbon dioxide or sulfur hexafluoride.^{12,13} In contrast to the permeation properties of conventional polymers, it was found that the mixed-gas selectivities of PTMSP can be higher than those obtained in pure gas permeation experiments.^{12,13}

The exact mechanism of separation has not been established for superglassy polymers such as PTMSP. However, we believe that because of its very high free volume (more than 20% of the polymer is open space), PTMSP acts more like an extremely finely microporous material than a normal solution-diffusion membrane. In a microporous material of this type, condensable vapors can adsorb onto the walls of the micropores, blocking transport of non-condensable gases. In another project, we have studied the separation of butane/hydrogen and butane/methane mixtures; the data support the micropore blocking mechanism. The application of PTMSP to nitrogen separation from natural gas is more complex. Low-grade natural gas contains nitrogen (a non-condensable gas), methane (a relatively non-condensable gas), and propane and butane (condensable gases). We believe that methane, propane and butane all condense within the micropores of PTMSP, blocking the permeation of nitrogen. The blocking effect becomes more pronounced at lower temperatures and with gas streams containing relatively high propane and butane concentrations.

A potential area of concern with PTMSP is membrane instability. Instability due to chemical degradation of the polymer (especially by oxygen) has been reported, but this is not likely to be a problem in this application. A second type of degradation is caused by the same phenomenon we propose to exploit—condensation of heavy hydrocarbons in the membrane.^{13,14} This type of degradation affects selectivity with permanent gas mixtures, such as oxygen/nitrogen, but should not be a problem with methane/nitrogen, where the property is being used to perform the separation required. An alternative to PTMSP as a selective material may be Teflon AF (poly(perfluoro-2, 2-dimethyl, 1,3 dioxole))¹⁵ another very high-free-volume polymer, which is reported to be stable.

Thus, the main thrust of the Phase I project was to evaluate these candidate polymers as potential membrane materials for this natural gas denitrogenation application.

2. PHASE I OBJECTIVES

The overall objective of Phase I was to develop high-performance membranes for the separation of nitrogen from natural gas, and to **identify** suitable process designs for this application. In the first part of the project, we determined whether methane/nitrogen **selectivities** can be improved by operating the membrane at lower temperatures, and if so, by how much. In the second part of the project, we performed an economic analysis of the membrane process and developed a number of process designs.

The specific objectives of the Phase I project were to:

1. Evaluate the separation characteristics of the membrane materials in the temperature range -30 oC to 22 oC, and under a variety of feed conditions.

Three polymer materials—silicone rubber, Pebax 2533 and PTMSP—were evaluated. Experiments were performed on membranes prepared from each material over the temperature range to evaluate the effect on the methane/nitrogen selectivity. Based on the results, PTMSP was selected for further evaluation. Tests were performed at feed pressures up to 1,000 psia, and for varying propane and butane concentrations in the feed gas. The data showed that silicone rubber and PTMSP both meet the target selectivity of 4-6 at -30°C.

2. Refine the membrane process design and **identify** means of lowering the total energy consumption.

The original process design was analyzed in detail; the analysis revealed that the energy consumption depends on the permeate pressure. Raising the permeate pressure from atmospheric to 100 psia reduces the net energy consumption substantially, without increasing the required membrane area significantly. An economic analysis showed that the membrane process is competitive with alternative technologies.

3. Select, based on the performance calculations and contacts with potential users, the most appropriate applications on which to focus scale-up work in Phase II.

Our survey of the potential users and industry experts confirmed that nitrogen separation from natural gas is an extremely important problem, and that development of a suitable low cost technology is a priority **need**. Based on conversations with potential users, we prepared a series of process flow diagrams, in which membranes were combined with other technologies as hybrid processes to maximize the overall efficiency of the separation. These hybrid processes, which are applicable over a wide range of feed nitrogen contents and flow rates, will be further developed in Phase II.

The experimental data obtained and the results of the economic analysis are described in the following sections.

3. EXPERIMENTAL TECHNIQUES AND PROCEDURES

3.1 Membrane/Film Preparation

Membranes based on the three selective polymers, silicone rubber, polyamide-polyether block copolymer (Pebax 2533), and PTMSP, were prepared.

Silicone rubber and Pebax 2533 were used to make composite membranes, with the structure shown in Figure 3. MTR prepares this type of membrane on a commercial scale with a permselective layer thickness of only 0.5-3 μm . In the Phase I work, however, we were principally concerned with membrane selectivity rather than membrane flux. No attempt to optimize the membrane thickness was made, therefore, and the composite membranes had a permselective layer thickness of 6 to 20 μm .

Figure 3. Schematic diagram of an MTR composite membrane.

The microporous support layer shown in Figure 3 provides mechanical support and a smooth coating surface for the permselective layer. The microporous substrate is formed by a casting process; its characteristics are determined by a number of factors including the nature of the backing paper, the solution viscosity, additives to the solution, and casting conditions. In a concurrent project, we have successfully optimized the microporous support to make it suitable for high-pressure natural gas-related applications.

The permselective layer, which performs the actual separation, must be thin and defect-free. Silicone rubber composite membranes were formed by coating a 6% solution of dimethyl siloxane in isooctane onto MTR's proprietary support membrane. The resulting silicone rubber had a nominal thickness of about 20 μm . After coating, the membrane was dried at 60°C to crosslink the membrane. The Pebax 2533 membrane was prepared from a 5% solution of the polymer in *n*-butanol solvent. The polymer solution was coated onto the support material and allowed to dry in the oven at 60°C. The membrane thickness was determined to be a nominal 6 μm .

The PTMSP membranes were prepared as homogeneous thin films. The flux of PTMSP is extremely high, and use of composite membranes with ultrathin PTMSP layers would have resulted in unreasonable gas usage during permeation tests. The film was prepared from a solution in toluene and allowed to dry first at atmospheric conditions and then in the oven at 80 °C. The nominal thickness of the film was about 30 μm .

3.2 Membrane Permeation Test System

A new test system was constructed to allow measurement of the permeation properties of the membranes at temperatures down to -60 °C. Due to the very high permeation fluxes of the membranes to be tested, this system also incorporated recycling of both residue and permeate streams to minimize the consumption of bottled gas. A diagram of the system is shown in Figure 4.

The test cell in the system is enclosed in an insulated box cooled with liquid nitrogen. The temperature box is controlled by a Resistance Temperature Detector (RTD) temperature controller coupled to a flow regulator on the liquid nitrogen tank. Tests with this apparatus demonstrated that -100 °C can be attained in approximately 5 minutes. The temperature gradient inside this box is negligible once this temperature is reached and is eliminated further by using a brushless fan inside the chamber.

The feed pressure to the membrane test cell can be maintained at 1,000 psig, using a Hom-Gas three-stage piston-type compressor. This device can compress methane up to 3,500 psig, at a maximum flow rate of about 2 scfm.

Figure 4. Flow diagram of low-temperature membrane testing system.

The construction of this test system took longer than expected; however, the completed system performed as expected and was very flexible in allowing us to meet all our testing conditions,

including low temperature, high pressure, flow rate, controllability of the chamber temperature and, most importantly, complete recycling of residue and permeate streams.

3.3 Experimental Protocol

A lean gas mixture comprising **10%** nitrogen, **3%** propane, and the balance methane, was used as a base-case gas mixture. All three membranes were tested at three different feed pressures at several different temperatures. Based on these data, the PTMSP membrane was selected for further evaluation. In these tests, the base-case gas mixture was made progressively richer in the higher hydrocarbons. Most experiments were carried out at 200 psia feed pressure and temperatures down to about -60°C. Some experiments were conducted at higher pressures up to 600 psia.

The feed, residue and permeate concentrations of methane, nitrogen and propane were measured by gas chromatography and the residue and permeate flow rates were also measured. The membrane separation properties were then calculated using our in-house cross-flow computer model,

4. EXPERIMENTAL RESULTS

4.1 Summary of Phase I Results

The most important experimental results of the Phase I program are summarized in Table 3, which shows the effect of temperature on the separation performance of the three membranes tested.

Table 3. Summary of Permeability and Selectivity of the Three Membranes Tested in Phase I.

Membrane Type	Feed Temperature (°C)	Methane Permeability Coefficient ($10^{-10} \text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$)	Membrane Selectivity (-)		
			CH_4/N_2	$\text{C}_3\text{H}_8/\text{CH}_4$	$\text{C}_3\text{H}_8/\text{N}_2$
Silicone Rubber	20	638	2.6	3.1	8.4
	0	461	2.9	4.1	11.9
	-35	411	4.0	7.5	30.0
Pebax 2533	22	12.5	2.8	3.0	8.4
	-35	0.175	1.6	3.2	5.1
PTMSP	20	1,716	3.0	4.2	12.6
	0	1,760	3.7	6.7	24.9
	-55	2,552	5.5	11.5	74.1

Figure 5 shows a plot of methane/nitrogen membrane selectivity obtained in a number of tests as a function of feed temperature for the PTMSP membrane. This plot shows clearly that the target methane/nitrogen selectivity of between 4 and 6 is achieved at temperatures below about -20 oC. Methane/nitrogen selectivities exceeding 5 were measured at temperatures below -50 oC.

Figure 5. Methane/nitrogen selectivity as a function of feed temperature for the PTMSP membrane.

The data in Table 3 and Figure 5 show that PTMSP and silicone rubber membranes are both good candidates for the separation of nitrogen from natural gas. Both achieve the target methane/nitrogen selectivity of 4-6 at -30°C required for a viable process, and both would give even higher selectivities at lower temperatures. Based on these results, we will continue to work with both materials in the Phase II project, making a final selection as more data become available.

4.2 Selection of Polymers

Six polymers were proposed as candidate materials: polyamide-polyether copolymer, an olefinic polymer, silicone rubber, poly(siloxylene-siloxane), PTMSP, and Teflon AF. Our preliminary evaluation of the properties of these materials showed that three of the polymers would not be viable choices for a commercial application. The olefinic polymer is likely to become too brittle on exposure to air for formation into spiral-wound modules. Poly(siloxylene-siloxane), which has promising methane/nitrogen selectivity at room temperature, is no longer commercially available. Preliminary permeation tests run with Teflon AF showed that this polymer is selective for nitrogen over methane. We selected the remaining three, listed in Table 4, for permeation tests, the results of which are reported in the following subsections.

Table 4. Membrane Materials Chosen for Feasibility Study for Denitrogenation of Natural Gas.
(Properties calculated from pure-gas measurements.)

Polymer Type	Methane Permeability ($10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$)	CH_4/N_2 Selectivity at 23°C
Rubbery polymers $T_g < -50^\circ\text{C}$		
Polyamide-polyether block copolymer (Pebax 2533)	20	4.2
Silicone rubber	760	3.3
Superglassy polymer $T_g > 150^\circ\text{C}$		
PTMSP	17,500	2.5

4.3 Silicone Rubber Membrane

The silicone rubber membrane was tested with the base-case mixture of methane, nitrogen, and propane at three different pressures and temperatures, Figure 6 shows the pressure-normalized flux of the three gases as a function of temperature at a feed pressure of 400 psia.

Figure 6. Effect of feed temperature on the pressure-normalized flux of propane, methane and nitrogen in silicone rubber at a feed pressure of 400 psia.

Figure 6 shows that the pressure-normalized fluxes of nitrogen and methane decrease with decreasing temperature, with the effect being more significant for nitrogen, whereas the pressure-normalized flux of propane increases with a decreasing temperature. This behavior shows that the decrease in the diffusion coefficients of methane and nitrogen match or exceed the increase in their volatility at lower temperatures. As a result, the pressure-normalized flux decreases slightly. For

propane, a condensable gas, the increase in the volatility is larger than the decrease in diffusion coefficient, resulting in a net increase in the pressure-normalized flux at lower temperatures.

The membrane selectivities, for propane/nitrogen, propane/methane, and methane/nitrogen, of the silicone rubber membrane are shown as a function of temperature in Figure 7. As shown, the selectivities increase with decreasing temperature.

Figure 7. Effect of feed temperature on the propane/nitrogen, propane/methane, and methane/nitrogen selectivity in silicone rubber.

The condensabilities of the three gases follow the order:

$$\text{propane} \gg \text{methane} > \text{nitrogen}$$

The propane/nitrogen selectivity increases approximately threefold from about 10 to 30 when the temperature is reduced from 22°C to -26°C. This selectivity increase is due to the increased volatility of propane at lower temperatures. The methane/nitrogen selectivity increases from 3 to 4. Extrapolation of the methane/nitrogen selectivity to lower temperatures suggests that, at an operating temperature of about -50°C, a methane/nitrogen selectivity of 5 could be obtained.

Based on these results, we conclude that silicone rubber is a potential candidate membrane material for a natural gas denitrogenation process. The material has a high permeability and an acceptable methane/nitrogen selectivity. Low temperature operation in the range -30 to -50°C would be required for a useful process,

4.4 Pebax 2533 Membrane

The effect of feed temperature on the pressure-normalized fluxes of methane, nitrogen and propane in Pebax 2533 membrane was determined with the base-case gas mixture. The results are shown in Figure 8. The trends with this membrane are different from those shown in Figure 6 for silicone rubber. The pressure-normalized fluxes of all three components decrease with decreasing

temperature. Also, the decrease in the flux is more rapid than for silicone rubber. Finally, the rate of decrease in the flux with decreasing temperature is in the sequence:

$$\text{propane} > \text{methane} > \text{nitrogen}$$

Figure 8. Effect of feed temperature on the pressure-normalized flux of propane, methane and nitrogen in Pebax 2533 at a feed pressure of 200 psia.

The trends in pressure-normalized flux shown in Figure 8 occur because the Pebax membrane is becoming glassy at lower temperatures. This is consistent with Pebax 2533 having a considerably higher glass transition temperature (T_g) than silicone rubber. At ambient temperatures (22°C), Pebax 2533 is rubbery, but the glass transition temperature must be somewhere in the range -20 to -30 °C. As the temperature of the permeation experiment is lowered, the membrane begins to convert from a rubbery to a glassy polymer. Figure 9 shows that the methane/nitrogen selectivity decreases with decreasing temperature. At lower temperatures, Pebax 2533 becomes less rubbery, and tends to become more nitrogen-selective. This results in a decreased methane/nitrogen selectivity. Similarly, the propane/nitrogen selectivity plummets at lower temperatures because the propane fluxes are affected more strongly than the nitrogen fluxes as the polymer becomes less rubbery.

Figure 9. Effect of feed temperature on the methane/nitrogen, propane/methane and propane/nitrogen selectivity in Pebax 2533.

Clearly, lowering the operating temperature to increase the methane/nitrogen selectivity of a rubbery membrane such as Pebax 2533 with a T_g close to the operating temperature is not feasible. Based on these results we conclude that Pebax 2533 is not a suitable candidate material for denitrogenation of natural gas.

4.5 PTMSP Films

The effect of feed temperature on the pressure-normalized fluxes of propane, methane and nitrogen in PTMSP, measured with the base-case mixture, is shown in Figure 10. The pressure-normalized flux of propane, the largest molecule, increases substantially at lower temperatures. The methane flux also increases, whereas the nitrogen flux decreases at lower operating temperatures. This is a very interesting and unusual result. Based on conventional knowledge of glassy polymers, a decrease in temperature typically lowers the permeation flux of all components due to a reduced diffusion coefficient. These results confirm that PTMSP is an unusual glassy polymer, which separates molecules by a mechanism different from that in conventional glassy membranes. We currently hypothesize that condensable components such as propane and butane are condensed into the open polymer framework of PTMSP, particularly at lower temperatures. Once these components are sorbed, the free volume in PTMSP is blocked, reducing the permeation flux of the lighter, noncondensable components such as methane and nitrogen. The result is the high propane/nitrogen selectivity as shown in Figure 11. The data in Figure 10 also indicate a slight increase in the methane permeation flux at lower temperatures. This increase could be due to increased sorption of the methane in the propane and butane already condensed/sorbed within the PTMSP free volume due to chemical interaction.

Figure 10. Effect of feed temperature on the permeation flux of propane, methane and nitrogen in PTMSP at a feed pressure of 200 psia.

Figure 11, Effect of feed temperature on the methane/nitrogen and propane/nitrogen selectivity of a PTMSP film.

These results are consistent with the separation mechanism for PTMSP at low temperatures discussed in Section 1.3. Propane is highly condensable and sorbs very strongly into the free volume of PTMSP, especially at low temperatures. As a result, the propane/nitrogen and methane/nitrogen selectivities increase as the operating temperature is lowered.

Figure 11 shows that reducing the operating temperature from about 20°C to -55 °C increases the methane/nitrogen selectivity from about 2.5 to about 5.5. Similar increases are observed for the propane/nitrogen and propane/methane selectivities. The high selectivity for propane over nitrogen is an additional benefit because it means that all the propane and higher hydrocarbons will also be recovered in a membrane process.

Based on these encouraging results for PTMSP, we measured the effect of feed temperature and propane concentration in the feed gas on the membrane flux and selectivity. The flux and selectivity are plotted against fractional saturation of propane in the feed gas in Figures 12 and 13. The fractional saturation of propane in the feed gas is defined as

$$\%Propane\ Saturation = \frac{P_F x_{propane}^F}{P_v^{propane}(T_F)} \times 100 \quad (2)$$

where P_F is the total feed pressure, $x_{propane}^F$ is the mole fraction of propane in the feed gas, and $P_v^{propane}(T_F)$ is the vapor pressure of propane in the feed gas, It is essentially the activity of propane in the feed gas multiplied by 100.

Figure 12 shows that, as the propane saturation of the feed gas is increased, the propane and methane fluxes increase, whereas the nitrogen flux is almost constant. The result is an overall increase in the hydrocarbon/nitrogen selectivity, as shown in Figure 13. The methane/nitrogen selectivity increases from about 2.5 at 2-3% propane saturation to about 5.5 at about 75% propane saturation,

Figure 12. Effect of the fractional saturation of propane in the feed gas on the permeation flux of propane, methane and nitrogen in PTMSP.

Figure 13. Effect of the fractional saturation of propane in the feed on the propane/nitrogen and methane/nitrogen selectivity in PTMSP.

As described in Section 1.3, an area of concern with PTMSP is membrane instability. We do not expect instability due to chemical degradation of the polymer to be a problem in this application. The second type of reported membrane instability is caused by condensation of heavy hydrocarbons in the membrane, which affects the membrane's selectivity with permanent gas mixtures, such as oxygen and nitrogen. It should not be a problem in methane/nitrogen separation, where the property is being used to perform the separation required.

In this project, we did not perform stability experiments with nitrogen-containing natural gas mixtures. However, experiments with hydrogen/hydrocarbon mixtures done in another project demonstrated that PTMSP membranes are stable; some data are shown in Figure 14. In this application, we have shown that PTMSP membranes maintain their flux and selectivity for several weeks. Thus, membrane instability, if it exists, is not a short-term problem. In permeation experiments with pure hydrogen, the initial very high permeability of PTMSP membranes decreases steadily, presumably because of loss of polymer free volume. When PTMSP is tested with butane/hydrogen mixtures, however, the hydrogen permeability is lower but remains constant for several weeks. We conclude that PTMSP membranes are stable in the presence of condensable hydrocarbons,

Figure 14. Permeability of PTMSP membranes with a hydrogen/butane mixture and with pure hydrogen in a prolonged test. The pure gas hydrogen flux of the membrane decreases with time, a phenomenon that is associated with loss of free volume of the PTMSP material. In tests with mixtures of hydrogen and a condensable vapor such as n-butane, the membrane is stable and extraordinarily permeable to the vapor component. This behavior is related to the condensation of the heavy hydrocarbon in the membrane material which maintains the material's free volume.

Based on the permeation properties of PTMSP, we conclude that PTMSP membranes are likely to be suitable for natural gas denitrogenation.

4.6 Laboratory-Scale Module Tests

Because the design and construction of the low-temperature full-recirculation test apparatus took longer than anticipated, we were not able to obtain laboratory-scale module performance data for methane/nitrogen separation during Phase I. Based on the amount of time required to construct the membrane stamp test system, we realized that modification of our bench-scale module test system for low temperature operation would also take a significant amount of time. Therefore, we decided to postpone all module tests to Phase II.

However, laboratory-scale spiral-wound PTMSP modules have been manufactured successfully for another project. These modules were tested with gas mixtures containing methane, ethane, propane and butane at feed pressures between 200 to 1,000 psig and temperatures of 25-30 °C. The objective was to obtain data for permeation fluxes of higher hydrocarbons. The modules performed satisfactorily and the data correlate well with that obtained in this Phase I project; therefore, we are confident that manufacturing spiral-wound modules from PTMSP will be straightforward. A description of our plan to test these modules in the Phase II project is given in Section 6.

5. ECONOMIC ANALYSIS

To determine the applicability of methane-selective polymers to natural gas denitrogenation, we performed a number of trial process design calculations for different types of natural gas streams. A key advantage of membrane systems is that they can be designed to handle large or small gas flows and a wide range of feed concentrations. The actual membrane process design for a specific methane/nitrogen separation plant will depend on the size of the gas stream and the nitrogen content of the gas. Broadly, the application area can be divided into the following four categories:

1. Low flow rate (2-20 MMscfd)/Low nitrogen content (4-10%)
2. Low flow rate (2-20 MMscfd)/High nitrogen content (>10%)
3. High flow rate (> 20 MMscfd)/Low nitrogen content (4-10%)
4. High flow rate (> 20 MMscfd)/High nitrogen content (> 10%)

In our economic analysis, we took as our base-case, a low-flow, low-nitrogen-content stream. We prepared a system design and analyzed the capital and operating costs for the system (see Section 5.1). A comparison with competing technologies was also made (see Section 5.2). Hybrid processes consisting of a membrane first stage followed by an adsorption, absorption or cryogenic second stage are likely to be a lower cost design for high-flow, high-nitrogen-content streams. Such designs are described in Section 5.3. Data from a Gas Research Institute database, summarized in Section 5.4, show that the size of the natural gas denitrogenation opportunity is large.

5.1 Economic Analysis of Membrane Denitrogenation Applications

Case 1: Design Study of Process to Produce Natural Gas Containing 4% Nitrogen

The cost of a membrane denitrogenation process depends on the selectivity and flux of the membranes as well as on the composition and flow of the gas to be treated. For the base-case analysis, we estimated the costs for a relatively small plant (5 MMscfd) designed to treat gas containing 8% nitrogen. The composition of the gas and the permeation flux of the membrane used in the analysis are shown in Table 5. The overall process flow scheme is shown in Figure 15.

Table 5. Gas Composition and Membrane Permeation Properties for Base-Case Economic Calculations (Case 1).

Gas	Methane	Ethane	Propane	Butane	Pentane	Nitrogen
% in Feed	75	10	4	2	1	8
Permeation Flux x104 (cm ³ (STP)/cm ² ·s·cmHg)	1	2	10	20	20	0.2

371B-1S

Figure 15 Single-stage membrane process utilizing available gas pressure to perform cooling and compression work for the separation of nitrogen from methane and for the recovery of natural gas liquids. Net hydrocarbon recovery includes methane and higher hydrocarbons.

The process scheme shown in Figure 15 comprises three main sections: 1) Natural gas liquids (NGL) recovery, 2) nitrogen/methane separation and 3) turbine compressor/expander. First, the raw feed gas is run countercurrent to the cold nitrogen stream from the turbine expander in a plate-fin heat exchanger. This cools the feed to below the dew point for some of the heavy

hydrocarbon components; these and additional hydrocarbons are removed by further cooling in an NGL dephlegmator. The cold feed gas is passed to a set of membrane modules cooled in an insulated cold box to enhance membrane selectivity. These methane-selective modules produce a nitrogen-depleted permeate gas that meets pipeline specifications and a residue enriched to 20-50% nitrogen or more. Both gas streams are then fed to a turbine expander/compressor where the permeate methane stream is repressurized to pipeline pressure and the high-pressure nitrogen stream is expanded and cooled to provide the refrigeration required to chill the incoming feed. This expansion also provides some of the work of compression for the product gas. The residue gas, containing approximately 20-50% nitrogen, is available as fuel for an engine to provide the additional power needed to compress the product gas back to pipeline pressure. In the case shown in Figure 15, the residue gas stream is capable of producing approximately 1,300 hp from an engine converting fuel heating to power at 20% efficiency. Since the compression power required in this case is only about 510 hp, this stream has more than adequate energy for the required compression of the product gas.

The estimated capital cost of the process is shown in Table 6. From this table, it is clear that the membrane costs are a small fraction (<10%) of the total plant costs, but compressor costs are significant. Thus, it is much more important to obtain membranes with high selectivity, rather than a high flux, because selectivity impacts product recovery and compression energy more strongly. Even if the membrane flux is half the target value shown in Table 5, operating costs increase by less than 10%. On the other hand, an increase in methane/nitrogen selectivity from 5 to only 5.5 would reduce the operating costs by at least 10%. It should be noted that we used a methane/nitrogen selectivity of 5 in these calculations as a conservative number even though a methane/nitrogen selectivity of about 5.5 was obtained in our experiments.

Table 6. Capital and Operating Costs of a 5-MMscfd Membrane Nitrogen-Removal Plant.

Capital Cost	
Membrane modules/pressure vessels at \$500/m ²	\$ 100,000
Product compressor at \$800/hp	408,000
Expansion turbine at \$2,000/hp generated	58,000
Frame/condensers/controls/insulation	300,000
	866,000
Engineering/assembly/installation at 60% of major capital components	520,000
Total Installed Cost	\$1,386,000 or \$277/Mscfd plant capacity
Operating Costs (350 days/year operation, 24 hours/day)	
Membrane Replacement 3-year lifetime (\$200/m ² module inserts)	\$ 14,000
Compressor power (obtained from nitrogen-rich gas stream)	0
Labor -1 operator at \$25/hour, 8 hours/day	73,000
Maintenance/parts (5% of capital equipment)	44,000
Capital recovery cost(22% of installed capital cost)	305,000
Total Plant Operating Cost	\$436,000 or \$0.30/Mscf produced
Other Debits/Credits	
Methane loss via nitrogen rich stream (\$1 .50/Mscf)	\$272,000
Natural gas liquids credits at \$0.15/gal	\$277,000
Processing Costs	\$43 1,000 or \$0.30/Mscf produced

The two main components of the overall energy consumed in the membrane process are the energy required to recompress the permeate stream, and the loss of methane in the residue stream. The cost of the compressor for the permeate stream is the largest capital equipment item, and is strongly dependent on the permeate pressure in the membrane system. By optimizing the permeate pressure, the cost of the compressor can be reduced, lowering capital and processing costs. Figure 16 shows the effect of permeate pressure on the capital cost and the processing cost of the system.

Figure 16. Effect of permeate pressure on (a) the capital cost and (b) the processing cost of the membrane system for the separation of nitrogen from natural gas. The feed to the membrane system corresponds to the base-case conditions shown in Table 5.

As shown in Figure 16(a), an increase in the permeate pressure results in a significant decrease in the capital cost due mainly to a decrease in the capital cost of the compressor for the permeate stream; that is, the total horsepower required to recompress the permeate stream decreases with an increase in the permeate pressure (i.e. the inlet pressure to the compressor). However, an increase in the permeate pressure has a counter effect as well. First, the membrane area required increases. However, since the membrane area is not a significant fraction of the capital cost, an increase in the membrane area does not negatively effect the capital cost. However, the other effect of increasing the permeate pressure is to reduce the recovery of methane while still producing pipeline quality natural gas (<4% nitrogen). This has an adverse effect on the processing costs, as shown in Figure 16(b).

Figure 16(b) shows that the processing cost passes through a minimum at a permeate pressure between 100 and 200 psia. As the permeate pressure increases from 50 psia to about 150 psia, the system capital cost decreases, which lowers the capital recovery cost and therefore the processing costs. The processing cost decreases from about \$0.40/Mscf to about \$0.26/Mscf. As the permeate pressure is increased further, the net recovery of methane decreases and becomes the dominant cost factor. This results in an increase in processing costs. The trade-off in the processing cost is between the size of the permeate recompressor, which decreases with increasing permeate pressure, and the cost of hydrocarbon loss in the membrane residue stream which increases with increasing permeate pressure. In the example shown in Figure 15, we used a permeate pressure of

100 psia because it combines a low processing cost with a relatively high net hydrocarbon recovery. The base-case economic calculations are shown in Table 6.

Overall, the estimated capital and operating costs for the membrane process are very encouraging. Plant operating costs are about \$0.30/Mscf of gas produced, which is significantly less than those of other processes, such as cryogenic systems, in this capacity range (see Section 5.2). More importantly, these costs are partially offset by the value of the recovered natural gas liquids. Taking this credit into account as well as the loss due to the value of the methane that is co-removed with the nitrogen, the processing costs total \$0.26/Mscf produced. It is important to note, however, that the methane recovery in the membrane system will typically be lower than in cryogenic systems,

The example shown in Figure 15 was calculated for a feed gas containing 8% nitrogen. As the nitrogen concentration in the feed gas increases, the total cost of the process per 1,000 scf of pipeline gas produced increases, principally because of the increasing amount of methane lost with the nitrogen-containing residue stream. At some point, the simple one-stage membrane design is no longer the lowest-cost process, and a second stage would be used to recover some of the methane lost in the nitrogen-containing residue gas, as shown in Figure 17.

In this design, the permeate from the first stage still contains more than 4% nitrogen, so the gas is recompressed to feed pressure and passed to a second membrane stage. The second-stage permeate then meets the pipeline specification. Even though the extra recompression and membrane stage increase the cost, our calculations show this process would still be attractive, particularly if there is a fuel use for the low-pressure, nitrogen-rich gas.

Figure 17. Two-stage membrane process for treating low-flow (2-20 MMscfd) high-nitrogen-content (> 10%) natural gas.

Case 2: Design Study of Process to Produce Gas of Heating Value of 1,000 Btu/scf

Many pipelines in the United States and worldwide now use the heating value of the gas as a criterion for the price paid. The gas has to be free of water and carbon dioxide and of other corrosive contaminants such as hydrogen sulfide, but higher levels of nitrogen are tolerable. Typically this heating value specification is between 950 to 1,050 Btu/scf. Gas of this heating value is suitable for most utility applications such as heating and power production in gas-turbine-based **cogeneration** plants. Membrane processes could be used for denitrogenation of low Btu gas to upgrade it to the required heating value specification while still recovering a significant amount of natural gas liquids,

Figure 18 shows a schematic diagram of a flowsheet to accomplish this separation. The process layout and the steps performed are as for Case 1 (Figure 15). The gas compositions are shown in Figure 18. The values of the membrane properties used in this study are the same as those used in Case 1. The estimated capital cost of the process is shown in Table 7.

Figure 18. Single-stage membrane process for denitrogenation of natural gas to upgrade heating value and recover natural gas liquids.

Table 7. Capital and Operating Costs for Denitrogenation of Low Btu Natural Gas for Upgrade to Pipeline Specification of 1,000 Btu/scf.

Capital Cost	
Membrane modules/pressure vessels (\$500/m ²)	\$ 195,000
Product compressor at \$800/hp	408,000
Expansion turbine at \$2,000/hp	97,400
Frame/condensers/flash/controls/insulation	300,000
	<u>1,000,400</u>
Engineering/assembly/installation at 60% of major capital components	600,240
Total Installed Cost	\$1,600,640 or \$320/Mscf
Operating Cost (350 days/year, 24 hours/day)	
Membrane replacement 3-year lifetime (@200/m ² module inserts)	\$ 26,000
Compressor power (\$0.03/kWh)	57,800
Labor (1 operator at \$25/hr, 8-hr/day)	73,000
Maintenance at 5% of capital	80,000
Capital recovery and interest cost at 22%	<u>352,100</u>
Total Plant Operating Cost	\$ 589,000 or 0.42/Mscf produced
Other Debits/Credits	
Hydrocarbon loss via nitrogen rich stream (\$ 1.5/Mscf)	\$ 85,600 or 0.059/Mscf
Natural gas liquids credit at \$0.15/gal	\$ 181,200 or 0.125/Mscf
Processing Cost	\$ 490,300 or \$0.35/Mscf produced

For this application, as for Case 1, the economics are very encouraging. The low processing cost of about \$0.35/Mscf produced is very competitive, especially in the flow rate range considered here. In addition, a membrane plant has numerous advantages over conventional processes such as cryogenic distillation, which requires significantly more equipment, resulting in higher cost.

As the power industry is deregulated, small-scale local production of power is likely to gain increased acceptance. This trend will be encouraged by the lower cost gas turbines now being produced. A nitrogen-contaminated reservoir can be profitably tapped as a fuel source for such local power generation plants provided some increase in the Btu value can be made at lower cost. Membrane processes would be ideal candidates for such applications because they can potentially deliver appropriate fuel at a reasonable cost using compact, low maintenance equipment.

5.2 Competing Technologies

Of the processes being considered for nitrogen removal from natural gas (see Table 2), cryogenic distillation is the only one being used on any scale. Twelve such systems are believed to be in operation in the U.S.¹⁶ Processing costs (including capital recovery cost, hydrocarbon losses and credits for NGL) for cryogenic plants vary with stream composition and size, but are in the range \$0.20 -0.33/Mscf for plants handling 75 MMscfd, and increase to more than \$ 1.00/Mscf for plants handling 2 MMscfd or less¹⁷. Other processes include pressure swing adsorption¹⁷ and lean oil adsorption^{7,18}. These two processes are even more expensive than cryogenic plants and have not found any significant acceptance by the industry.

Cryogenic processes are typically used to treat gas containing more than about 10% nitrogen, but the need for extensive pretreatment is a major drawback. Pretreatment generally consists of amine scrubbing to remove carbon dioxide followed by glycol dehydration to remove most of the water vapor, Molecular sieves then remove any remaining water vapor and carbon dioxide, after which the gas is cooled in a final polishing step to remove heavy hydrocarbons and aromatics. All of these components must be removed to avoid freeze-up in the cryo-section of the plant, which operates at -150 °C. The gas leaving the pretreatment plant is cooled and liquefied in a series of operations involving expansion across Joule-Thompson valves, for a low-pressure product, or across expansion turbines, for a high-pressure high-quality final product. Depending on the feed conditions and the final disposition of the products, each cryogenic system is custom-designed. The complexity of the pretreatment makes operational reliability a concern. A simpler, more reliable pretreatment process would make cryogenic processes much more attractive.

In the pressure swing adsorption (PSA) process, methane and other hydrocarbons are adsorbed onto molecular sieves, leaving a nitrogen-rich gas stream¹⁷. The PSA process is most competitive, therefore, for feed streams containing a high concentration of nitrogen. Multiple beds are typically used, with complicated switching controls between beds. The capital and operating cost of these systems are relatively high. In general, PSA processes are suited to low to medium gas flows.

Lean oil absorption processes, such as the Mehra process,¹⁸ have been under development for about 10 years. These processes use chilled oil to absorb methane and other hydrocarbons. The oil is then heated and flashed at lower pressure in a series of vessels, and the liberated hydrocarbon gases are collected and recompressed to pipeline pressures. High recovery of hydrocarbons is achieved, but the process is capital intensive. As with PSA, the process is best suited for throughputs of less than about 10 MMscfd with relatively high nitrogen concentrations.

Finally, an absorption process based on nitrogen-chelating chemicals has been reported recently. A solvent containing a chelating agent absorbs nitrogen from the natural gas, leaving the methane and other hydrocarbons behind. This process is the early development stage. The chelating agents are expensive and of questionable stability, problems that are likely to be exacerbated under gas field conditions.

Table 8 compares the membrane process with currently available technologies for the separation of nitrogen from natural gas containing 8% nitrogen. The lean oil adsorption technique, applicable to higher nitrogen content streams, would have a capital cost of \$2.13 million and an operating cost of \$2.37/Mscf if used on a stream containing 25% nitrogen.

Table 8. Cost Comparison for Various Technologies Currently Available for Removal of Nitrogen from Subquality Natural Gas. These costs reflect a throughput of 1-5 MMscfd of natural gas. In this range, the conventional processes are severely disadvantaged due to economies of scale. In the higher, 75 MMscfd range, the costs for PSA and cryogenic distillation are significantly lower.

Technology	8% Nitrogen	
	Total Capital Cost* (\$/Mscfd plant capacity)	Processing Cost (\$/Mscf)
Cryogenic Distillation	1,184	1.30
PSA	1,320	1.65
Membranes	277	0.30

*Cost figures from Reference 17. The PSA and cryogenic distillation costs were interpolated from 6 % and 15% nitrogen cases in Reference 17.

The cost comparison in Table 8 for cryogenic, PSA and membrane processes for treating nitrogen-containing natural gas is for flow rates less than 5 MMscfd. Clearly, the membrane process has significant cost advantages over existing technology in this flow range. However, as the flow rate treated increases, the relative cost of cryogenic and PSA decreases quite dramatically, whereas that of the membrane process is almost unchanged. At higher flow rates, therefore, the membrane process would be less economical than cryogenic and PSA, especially since the recovery rates of methane in these conventional technologies are likely to be higher.

At high throughputs, it is likely that hybrid processes using membranes as bulk separators and conventional technologies for product polishing and recovery would be most feasible. We intend to study the potential of these hybrids in Phase II.

5.3 Hybrid Designs

Discussions with potential end-users of the process suggest that combination of a membrane separation process with other natural gas separation technologies would maximize the overall

efficiency of the separation, particularly for higher flow, high nitrogen content streams. Three such options are described below.

Low Flow Rate/High Nitrogen Content

An alternative configuration to the two-stage membrane system shown in Figure 17 for low-flow-rate/high-nitrogen-content streams is the hybrid design shown in Figure 19. This process combines a first-stage membrane system as a pretreatment/bulk separation step with lean oil absorption for further recovery of methane and hydrocarbons from the membrane residue stream. The membrane process reduces the volume of the feed gas by approximately 50% by preferentially removing methane. The nitrogen-rich residue stream then contains 44% nitrogen and is cold and at pressure, ideal conditions for the absorption process. Thus, the membrane and absorption processes both work in their optimum operating range. The refrigeration used to cool the gas going to the membrane stage is used advantageously by the absorption stage because both work most efficiently at low temperatures.

Figure 19. Hybrid process combining a single-stage membrane system with an adsorption process for treating low-flow, high-nitrogen-content natural gas.

One advantage of the hybrid process shown in Figure 19 over the two-stage membrane design illustrated in Figure 17 is that methane recovery is likely to be high, on the order of 95% or more. Methane loss with the nitrogen gas stream becomes increasingly important as the size of the plant increases. Figure 19 shows a membrane/absorption hybrid, but a membrane/PSA hybrid could also be used.

High Flow Rate/Low Nitrogen Content

For large gas streams contaminated with low levels of nitrogen, our calculations suggest that the best process is a single-stage membrane unit followed by lean oil absorption or PSA to increase methane recovery, as shown in Figure 20.

This hybrid scheme has significant advantages over either process alone. The membrane step separates the bulk of the methane from the natural gas. The residue gas passed from the membrane system to the adsorption unit has a smaller volume and is enriched in nitrogen. It contains none of the other contaminants present in natural gas, namely, carbon dioxide, hydrogen sulfide, higher hydrocarbons, water vapor, etc. because these permeate the membrane with the methane stream. This enables the adsorption process to work at maximum efficiency. The gas is also at pressure, which is required by the adsorption system. The adsorption process selectively adsorbs additional methane in the natural gas, and rejects an essentially hydrocarbon-free nitrogen stream. A two-stage membrane process of the type illustrated in Figure 17 is also possible, but recovery would be lower than with the hybrid plant.

Figure 20. Hybrid membrane/adsorption process for treating high-flow, low-nitrogen-content natural gas streams.

High Flow Rate/High Nitrogen Content

Many major fields in the United States and around the world fall into this category; most are not currently exploited due to a lack of available processing technology. An all-membrane design would not provide the high methane recovery required for large flows with high nitrogen content. A membrane/adsorption or absorption hybrid could be used, but the large volume of gas to be treated is likely to be outside the optimum range for the non-membrane process. For these reasons, we believe the best process for these streams is a membrane/cryogenic hybrid as shown in Figure 21. The membrane unit both performs a partial separation of nitrogen from the gas and removes all of

the water, heavy hydrocarbons, carbon dioxide and hydrogen sulfide from the gas, The remaining methane/nitrogen separation is performed by a cryogenic plant.

The process shown in Figure 21 has significant advantages over the cryogenic process alone. First, by performing a bulk separation, the small membrane system (only 1,250 m² in membrane area for 50 MMscfd) reduces the flow of gas to the cryogenic plant by about 30%, reducing the size of this unit substantially. More importantly, however, the membrane system largely eliminates the complex, costly pretreatment train required in a cryogenic plant to remove all condensable components. Such trains comprise several processes, including chemical absorption to remove carbon dioxide and hydrogen sulfide, LPG condensers and stabilizers to remove higher hydrocarbons, and glycol dehydration combined with polishing by molecular sieve adsorption to remove water. In the proposed hybrid process, a single membrane separation step replaces the pretreatment train. This is possible because the membrane is permeable to carbon dioxide, hydrogen sulfide, water vapor and higher hydrocarbons in the feed gas, as well as to methane. Elimination of a complex pretreatment train will reduce the cost of cryogenic distillation significantly, especially for large gas streams, and will increase the reliability of the overall process.

Figure 21. Hybrid membrane/cryogenic distillation process for treating high-flow, high-nitrogen-content natural gas.

5.4 Size of Denitrogenation Application

To identify and classify natural gas formations and fields prone to nitrogen contamination, we performed a survey based mainly on the gas composition database prepared by Energy and Environmental Analysis Inc. for the Gas Research Institute.² The data that relate to natural gas classified as low-quality due to the presence of nitrogen are summarized below.

In 1988, about 26% of the total natural gas *production* of 14 trillion cubic feet (TCF) was low-quality due to the presence of either or both carbon dioxide and nitrogen. About one-third of this 26% was **subquality** due to nitrogen concentrations higher than 4%. Of a total of 143 TCF of known natural gas *reserves* in 1988, 34% was subquality. Of this, 40%, or about 14% of the total reserves of 143 TCF, was subquality due to high nitrogen content. Thus, in 1988, about 9% of the production was subquality in nitrogen content, and about 14% of the reserves were classified as subquality with respect to nitrogen.

Figure 22 shows the distribution of nitrogen concentration as a **function** of the volume of the reserves. As shown, the concentration of nitrogen in subquality natural gas can be as high as 20%, and the bulk of the contaminated reserves contain between 5 and 18% nitrogen. As described above, the entire range of these concentrations can be effectively treated to produce pipeline quality natural gas using membrane only or membrane hybrid processes.

Figure 22. Reserves volume as a function of nitrogen concentration in natural gas. Nitrogen concentrations more than 4% are considered subquality.

Table 9 gives the regional distribution of the high-nitrogen reserves in non-associated natural gas. As the table shows, the major nitrogen-prone reserves are located in the Mid-Continent and the Rocky Mountain Foreland regions. In the Mid-Continent region, the Anadarko basin, including the Hugoton field, is the most important area of nitrogen occurrence, with the nitrogen being concentrated in the Permian and Pennsylvanian sections and the Hugoton Embayment area. In the Rocky Mountain area, high nitrogen occurs with high carbon dioxide and hydrogen sulfide in the Paleozoic of the Green River Basin area. Newer fields are expected to be mostly in formations in the Mid-Continent and Rocky Mountain regions. Since the formations in these regions contain substantial amounts of subquality gas, the need for economically viable advanced processing techniques is clear.

Table 9. Distribution of Non-Associated Gas with 4% or more Nitrogen in 1988 Reserves.²

Region	High Nitrogen Natural Gas (TCF)
Mid-Continent	15.31
Rocky Mountain Foreland	3.61
Arkla-East Texas	1.67
Permian Basin	0.94
West Coast Onshore	0.89
Williston Basin	0.4
Midwest	0.3
Appalachia	0.1

6. BENCH-SCALE TEST PLAN

The Phase II portion of the project will have two components: laboratory tests of modules and field tests of modules. Laboratory-scale modules will be tested in our bench-scale module test system; a diagram of this system is shown in Figure 23. For this project, the system will be modified for low-temperature operation,

Figure 23. Flow diagram of the existing bench-scale test apparatus for determining the performance of membrane modules. The maximum feed pressure is 1,500 psig, and the maximum feed flow rate is 11 scfm. System will be modified for low-temperature operation.

This system is a total recycle system for performing continuous separation tests on spiral-wound modules. It is equipped with a two-stage 7.5-hp diaphragm compressor that can deliver up to 11 scfm flow at pressures up to 1,500 psig. The gas is introduced into a high-pressure vessel containing the module. The residue gas is reduced in pressure and mixed with the permeate gas before being recompressed by a small diaphragm compressor to about 30 psig. This combined stream forms the feed gas to the larger compressor. In this system, both residue and permeate streams are recycled so that no gas loss occurs. The test system has an on-line GC sampling loop so that feed, residue, and permeate streams can be sampled continuously. The gas chromatography is a P200H portable TCD detector GC built by MTI (Fremont, CA); this GC can give a complete natural gas analysis (C_1 to C_{20}) within two minutes. The test system is also equipped with inlet ports that allow injection of various heavier hydrocarbon into the flow loop.

We plan to evaluate modules containing silicone rubber membranes, PTMSP membranes and membranes prepared from at least one other superglassy polymer in preliminary base-case tests and then to decide which type of module to test further. Currently, we believe that the PTMSP membrane or a similar superglassy membrane presently under development at MTR will be used for this separation.

Table 10 shows the key operating parameters we propose to study in this bench-scale module test program. The variables listed in Table 10 are chosen because operating conditions for the membrane process will fall within the given range of temperature, pressure and flow conditions.

Table 10. Parameters for Phase II Bench-Scale Module Test Program

Parameter	Base Case	Variations
Feed Pressure (psig)	600	200, 1,000
Feed Temperature (oC)	-50	-60,-25
Feed Flow Rate (scfm)	10	4, 7
Feed Propane Saturation (%)	75	50,90

The specific experiments we propose to conduct during the Phase II laboratory module evaluation are:

- 1) Preliminary experiments with different module types

Each module will be tested at the base-case conditions plus the feed temperature and pressure variations listed in Table 10, that is, a total of nine experiments per module. Each experiment requires about two hours of steady-state operating and multiple readings of pressures, temperatures, flow rates and stream compositions. We anticipate that two experiments can be completed in one day, so tests of three different modules will take about one full man-month, including data analysis. During Phase II of the

project, we expect to perform preliminary testing with at least five modules. At the conclusion of this preliminary testing, we will select the best membrane and proceed with full parametric testing.

2) Full parametric testing

At least three modules will be prepared with the membrane selected from the preliminary tests for full parametric testing at the base-case conditions plus the pressure, temperature and propane content variations listed in Table 10. The feed flow rate variations will only be performed at the base-case condition, This totals 29 experiments per module, which we estimate will take one full man-month, including data analysis.

The data from these tests will be analyzed to produce, through extrapolation, expected membrane performance characteristics under realistic operating conditions with 8-inch spiral-wound modules, The data will also show the effect of specific internal components/configurations of the modules on the gas separation achieved, This information will be used to appropriately **modify** and scale up **the** modules first to 4-inch and then to 8-inch commercial-scale spiral-wound modules,

In the second part of Phase II, we plan to test these modules under realistic field conditions, if appropriate sites can be arranged. Although field testing is not a required part of Phase II, we believe that it will provide valuable real-life experience on the effects of various gas components on membrane performance and life. Such tests will also allow us to operate the smaller modules under flow conditions equivalent to those of a full commercial installation, A P&I diagram of the test skid we intend to modify for the field tests is shown in Figure 24.

This test skid for natural gas applications is designed for a 150-scfm feed stream. Only two significant modifications are needed for this application. To allow operation at temperatures from ambient to -50 oC, the existing 3-inch diameter module housing will be fitted with a refrigerant cooling jacket insulation and a 0°C to -60oC low-temperature chiller. The other modification is to install an 8-inch module housing on the rack,

The test skid will separate a natural gas feed into a nitrogen-enriched residue and permeate enriched in methane and higher hydrocarbons. These streams will be sampled and analyzed by gas chromatography. The permeate and residue streams will be returned to the process train at appropriate pressure points. The system will be configured so that two sets of membrane modules can be evaluated simultaneously by monitoring the gas flow and composition of the respective feeds, residues and permeates separately.

Figure 24. Flow diagram, showing pressure (P), temperature (T), and flow (F) monitoring points, of the field test skid for the evaluation of 3-inch and 8-inch modules for the removal of nitrogen from natural gas.

A complete test plan for the field test will be prepared after the test site has been negotiated. The key variables of interest to us to help in developing the modules and process are the feed flow rate and pressure. The effect of these variables on the separation performance of the module will be determined. The other key objective of the field test is to determine the effect of trace components and contaminants in the natural gas on the separation performance of the modules.

The data obtained from the bench-scale tests and from the field test will then be used to determine the most suitable applications for the membrane technology and to develop a more detailed economic analysis on these applications. The manner in which these analyses will be performed are detailed in Tasks 16 and 17 of the original proposal.

7. CONCLUSIONS

Phase I of the project demonstrated the technical and economic feasibility of using methane-selective membranes for natural gas denitrogenation. The following conclusions can be drawn from the Phase I results:

1. Our calculations show that a methane/nitrogen selectivity of 4 to 6 is required for economical separation of nitrogen from natural gas by a membrane process. The Phase I work showed that two polymers, silicone rubber and PTMSP, have this selectivity under appropriate operating conditions.
2. PTMSP has a methane/nitrogen selectivity of 5.5 at -55 °C. PTMSP membranes have even higher permeabilities than silicone rubber. On the other hand, PTMSP'S permeation properties are affected by the presence of other components in the gas such as propane and butane, and this dependence has not been completely determined. Also, although our work shows PTMSP to be stable at the high-pressure conditions of natural gas plants, the literature contains a number of reports suggesting PTMSP is unstable because of slow loss of free volume. Work on these membranes will also be continued in Phase II.
3. The results of two design studies and economic evaluations are very encouraging. Both analyses were based on properties of a membrane with a methane/nitrogen selectivity of 5 and treating 5 MMscfd of nitrogen-containing natural gas.

To treat a gas stream containing 8% nitrogen to lower the content to 4% in the product gas, the membrane system shows an installed capital cost of \$1.4 million. The plant operating expenses are \$0.30/Mscf treated. Accounting for unrecovered methane in the membrane reject stream and taking credit for the NGL recovered, the net processing cost for producing pipeline quality natural gas is about \$0.30/Mscf. To treat a gas stream containing 30% nitrogen to produce natural gas with a heating value of 1,000 Btu/scf, the total installed cost of a membrane system is \$1.6 million and the operating cost is \$0.421 /Mscf produced. Taking into account methane loss and credits for NGL recovered, the process cost for this application is \$0.35/Mscf.

The economics of both applications are very attractive and competitive with existing technologies. An important aspect of these numbers is that membrane processes can treat smaller throughputs of natural gas of up to 10-15 MMscfd economically. As the flow rate to be treated increases, economies of scale favor conventional technologies such as cryogenic distillation. The membrane-based process not only produces pipeline quality natural gas, but also produces natural gas liquids which command a premium price over the gas.

4. Hybrid processes combining membrane systems with other natural gas treatment technologies are likely to be more economically attractive for larger streams with a high nitrogen content.
5. The size of the opportunity is large; about 14% of natural gas reserves are subquality with respect to nitrogen content.

REFERENCES

1. D. Leppin and H.S. Meyer, "Gas Research Institute Program in Natural Gas Processing' GRI,SPE21505, presented at SPE Gas Technology Symposium, Houston, TX (Jan, 23-25, 1991).
2. R.H. Hugman, E.H. Violas and P.S. Springer, "Chemical Composition of Discovered and Undiscovered Natural Gas in the U.S. Lower-48," Executive Summary, GRI, Tightsands and Gas Processing Dept. (March 1993).
3. H.D. Shoemaker, C.J. Brinker, and R. Sehgal, "Fundamental Studies for Sol-Gel Derived Gas-Separation Membranes," Proceedings of the Natural Gas RD&D Contractors Review Meeting, Volume II, p. 409, Baton Rouge, LA, (April 1995).
4. S. A. Stern, "Polymers for Gas Separations: The Next Decade," J. Memb. Sci. **94**, 1 (1994).
5. W.J. Koros and G.K. Fleming, "Gas Separation Using Membranes Thin Film Composite Membrane," Membrane Based Gas Separations, Annual Reviews of Memb. Sci., Vol. I, 1, Elias Klein (cd.),NAMS(1993).
6. S.A. Stern, V.M. Shah, and B.J. Hardy, "Structure Permeability Relationships in Silicone Polymers," J. Polymer Sci: Polymer Physics Ed. **25**, 1263 (1987).
7. T.H. Kim, W.J. Koros, C.R. Husk, and K.C. O'Brien, "Relationship Between Gas Separation Properties and Chemical Structures in a Series of Aromatic Polyamides," J. Memb. Sci. **37**, 45 (1988).
8. M.R. Coleman and W.J. Koros, "Isomeric Polyamides Based on Fluorinated Dianhydrides and Diamines for Gas Separation Applications," J. Memb. Sci. **50**,285 (1990).
9. K. Tanaka, H. Kita, M.Okano, and K. Okamoto, "Permeability and Permselectivity of Gases in Fluorinated and Non-Fluorinated Polyamides," Polymer **33**, 585 (1 992),
10. T. Masuda, E. Isobe and T. Higashimura, "Poly[1-trimethyl(silyl)- 1 -propyne]: A New High Polymer Synthesized with Transition-Metal Catalysts and Characterized by Extremely High Gas Permeability," J. Am. Chem. Sot. **105**,7473,7474 (1983),
11. S. Auvil, R. Srinivasan, and P.M. Burban, "Mechanisms of Gas Transport in Poly(1-trimethylsilyl-1-propyne)," Polymer Preprints **32**,380 (1991).
12. L.G. Toy, I. Pinnau, and R. W. Baker, "Gas Separation Process," U.S. Patent 5,281,255 (January 25, 1994),

13. T. Nakagawa, T. Saito, S. Asakawa, Y. Saito, "Polyacetylene Derivatives as Membranes for Gas Separation," Gas Sep. and Purification 2,3 (1988).
14. Yu. P. Yampol'skii et al., "Transport Characteristics and Other Physiochemical Properties of Aged Poly(1-(trimethylsilyl)-1-propyne)," J. Appl. Pol. Sci. 48, 1935 (1993).
15. S.M. Nemser, "Air Intake System for Mobile Engine," U.S. Patent 5,147,417 (September 15, 1992)
16. C.C. Tannehill and C. Galvin, "Business Characteristics of the Natural Gas Conditioning Industry," Topical Report to GRI, No. GRI-93 10342 (1993).
17. M.K. Changela, R.L. McKee, H. Heshan, V.K. Pathak, M.D. Quinlan, and J.F. Strickland, "Evaluation of Natural Gas Process Technology," L.W. August 7, 1996 Echterhoff and G.J. Reading (eds.) (The M.W. Kellogg Co.), Topical Report, Task 3, Vol. II., Topical Report to GRI, No. GRI-91 10230 (Sept. 1990).
18. Y. Mehra, "New Process Flexibility Improves Gas Processing Margins," Energy Progress, 7(3), 150 (Sept. 1987).