Methane Selective Membranes for Nitrogen Removal from Low Quality Natural Gas – High Permeation Is Not Enough

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ABSTRACT

Nitrogen is very difficult to remove from natural gas. Most specifications require no more than 4% nitrogen or total inerts in the interstate pipeline system. With about 15% of the raw natural gas produced in the United States having nitrogen contents over 4%, technology is needed to economically bring the gas to pipeline quality. Cryogenic distillation, the current state-of-the-art technology, is expensive, especially in smaller applications. Lean oil systems, such as AET's Mehra Process, and pressure swing adsorption processes, such as Nitrotech's carbon molecular sieve and Engelhard's Molecular Gate, are being applied in very limited cases. Membranes are in the development stage for such applications.

A development program based on a rubbery membrane that had very high methane permeation rates was planned. Unlike carbon dioxide/methane separation membranes, methane molecules permeate faster than nitrogen. Methane/nitrogen selectivity, the ratio of permeation rates, is about 3, compared to carbon dioxide/methane selectivity of 15-80 for glassy membranes. It was suggested that the very high permeation rates and resulting lower capital costs would offset compression requirements. A nonlinear program, based on Qi and Henson, was posed as the minimization of the total annual cost subject to constraints imposed by the separation requirements and operating conditions. We used the nonlinear program solver CONOPT within the Generic Algebraic Modeling System (GAMS) to solve the optimal design problems.

The economic study results as the nitrogen content, selectivity, and several membrane configurations, including single stage, two-stage, two-stage with permeate recycle, two-stage with residual recycle, and three-stage with permeate and residual recycle. Significant increase in selectivity is required before any configuration would be economic.

INTRODUCTION

Projections clearly indicate that demand for natural gas is rising and that there is an increasing need to develop the capability to upgrade subquality gas sources, which tend to exist in relatively small quantities in remote areas. Nitrogen (N_2) and carbon dioxide (CO_2), two components of natural gas common to a number of producing basins, are

noncombustible contaminants that typically must be removed before gas can be sold. Processes exist for the removal of both contaminants down to pipeline specifications; however, much of the domestic natural gas processing is conducted in large-scale plants to obtain the cost benefits of economies of scale. Low-cost methods are still needed for improving the quality of relatively small volumes of gas produced far from major processing centers.

One technology that holds promise for remote, low-volume applications is the use of selectively nonporous membranes to separate gas contaminants. Conventional glassy polymer membrane materials, such as cellulose acetate and polysulfone, separate gases based generally on differences in their molecular sizes, and have been shown, in previous GRI-supported studies, to be effective at separating CO_2 from high-CO_2 content natural gas. However, because methane and nitrogen are nearly identical in size, conventional membrane technology cannot be used to effectively separate N_2 from high-N_2 content natural gas. For these reasons, membrane-based separation of N_2 has been pursued with particular focus on silicone membranes, which differ from glassy polymers in that they separate transport gases by sorption rate differences rather than by diffusion rates. A gas under pressure will liquefy on the surface of a silicone film, dissolve into it, and diffuse as a dissolved gas to the opposite surface where it will revaporize and escape as a gas. Both gases diffuse rapidly through the membrane, but because gases have different rates of solubility in silicone, a silicone membrane can separate them effectively. Methane dissolves more readily in silicone than nitrogen. For these methane-selective membranes, however, the permeated methane is at a lower pressure than the feed gas, requiring recompression of the hydrocarbon stream. This is due to the pressure drop across the membrane that provides the driving force for the separation.

Efforts to develop polymeric membranes for use in the separation of mixed gases started in the 1970s by many companies, including General Electric, Dow Corning, and UOP. Despite these efforts however, it proved virtually impossible to develop a practical silicone membrane. The main difficulty was the inability to produce an ultrathin silicone film that was nonporous. Ultrathinness of the membrane material is essential to make the gas separation cost effective, especially for the case of N_2 separation from natural gas. Membrane Technology & Research (MTR) later achieved some limited success in the development of a "silicone/polysulfone composite membrane." However, by the nature of its composite materials, MTR's membrane compromise both the permeability and selectivity, greatly effecting cost effectiveness. MTR has recently patented several configurations to utilize combinations of nitrogen- and methane-selective membranes for economic natural gas systems.

In recent years, an independent inventor who claimed to have developed a practical silicone membrane targeted for the separation of N_2 from natural gas in a cost-effective manner approached Gas Technology Institute (GTI). While details pertaining to this work are proprietary, preliminary results strongly hint to success in the development of a nonporous, ultrathin silicone composite membrane, with silicone film thickness as thin as one micron or even thinner that is fully capable of separating N_2 from natural gas. Prior

to initiating an expensive research program, process economics were first developed to justify and prioritize the research.

Optimal gas separation system designs were derived for methane selective membranes with various nitrogen permeabilities and CH_4/N_2 selectivities. MTR's patent (Baker et al., 1997) was used in the comparative economic analysis as the BASE CASE and provided property and operating conditions for this study. As compared to the BASE CASE membranes, the PROPOSED membranes have a very high N_2 permeability but a low CH_4/N_2 selectivity. The objective of this study was to evaluate the economic tradeoffs associated with these two membrane materials cases. This was achieved by deriving optimal designs for selected membrane system configurations previously studied for natural gas upgrading (Qi and Henson, 1998).

DESIGN BASIS

The membrane permselectivity properties, feed conditions and separation requirements were obtained from examples presented in the patent. Some parameter values required for the membrane permeator model (Qi and Henson, 1996) and the economic model (Qi and Henson, 1998) were not available in the patent. Unknown permeator model parameters were assigned values that yielded reasonable results, while unknown economic model parameters were assigned values used in previous publications (Qi and Henson, 1998). With the exception of the membrane properties, the design basis for the proposed membrane separation systems was chosen to be identical to that for the BASE CASE. The permselectivity properties of the PROPOSED membrane were obtained from the inventor.

Generally the system had a 5 MM scfd feed stream containing 80 or 90% CH_4 and 10 or 20% N_2 at 1000 psig. The product stream must be at least 96% CH_4 and returned to 1000 psig. As a conservative assumption, the permeate side pressure drop parameter was taken to be null for computational ease throughout the analyses. Worse separation performance would be expected if the permeate pressure built up.

The parameters used in the study are listed in Table 1.

Table 1: Parameters for Membrane System.

Parameter	Units	Value
Capital charge	%/year	27
CH_4 value	$/M scf	3.00
CH_4/N_2 selectivity	-	3.1
Compressor capital	$/kW	1073
Compressor efficiency	%	33
Feed composition - Multiple Stage	% CH_4	80
Feed composition - Single Stage	% CH_4	90
Feed flow rate	MM scfd	5
Feed temperature	F	68
Inlet Feed pressure	psig	1000
Maintenance	%	5
Membrane housing	$/ft^2	46
Membrane lifetime	years	3
Membrane replacement	$/ft^2	18
N_2 permeability – Multiple Stage	mol/MPa/m^2/s	75
N_2 permeability – Single Stage	mol/MPa/m^2/s	0.03
Permeate composition	% CH_4	> 96
Permeate pressure	psig	14.7
Working capital	%	10
Working days	days/year	350

OPTIMIZATION METHODOLOGY

The economics of the BASE and PROPOSED membrane materials were compared by deriving optimal process designs for predetermined system configurations. In this context, a membrane separation system consists of membrane permeators, recycle gas compressors, and stream splitters and mixers. A separation stage represents a single permeator or several permeators in parallel as required by the membrane area. The system configurations were predetermined in the sense that the interconnections between the permeators and compressors were specified prior to performing the optimization.

The optimal process design problem was posed as the minimization of the total annual cost subject to constraints imposed by the separation requirements and operating conditions. In all the problems discussed in the following section, constraints were enforced on the minimum CH_4 composition of the product stream and the permeate pressure at the outlet of each separation stage. Model equations for the membrane permeators (Qi and Henson, 1996) and material balances were included as additional constraints. The cost function includes terms for: (1) capital investments associated with membrane housing and gas compressors; and (2) operating costs for membrane replacement, compressor utilities and CH_4 lost in the waste stream. Due to the approximate nature of the cost function, the methodology is best suited for comparing the relative economics of various process designs rather than determining an accurate cost for a particular design.

The resulting optimization problem is commonly known as a nonlinear program. In this work, the nonlinear program solver CONOPT within the Generic Algebraic Modeling System (GAMS) was used to solve the optimal design problems. A solution yields the process cost, the stream flow rates and compositions, and the membrane area and compressor power associated with each separation stage. Some care must be exercised when interpreting the results, as the nonlinear program is non-convex due to the permeator model equations. The practical implication is that the solution may represent only a local minimum of the nonlinear program. In an attempt to obtain the global minimum, the nonlinear program was resolved from various initial conditions until some confidence was gained that the solution obtained most likely represented the global minimum. Additional details on the formulation and solution of the optimal design problem are available elsewhere (Qi and Henson, 1996).

Unless stated otherwise, the nominal values for the operating conditions and membrane properties were obtained from Example 2 of the MTR patent (Baker et al., 1997). As discussed below, the feed and permeate pressures were determined such that the optimization results matched those in Example 2 of the patent. The parameter that determines the amount of pressure drop on the permeate side of the membrane permeator was taken to be zero as explained below. This is equivalent to assuming no permeate side pressure buildup. Unless stated otherwise, the nominal values for economic parameters were obtained from Example 10 in the patent. Because there are no direct analogs to the capital charge and working capital in the economic model used in the patent, nominal values for these parameters were obtained from a previous study on natural gas upgrading by the consultant (Qi and Henson, 1998).

The following outputs from the optimization code are used to evaluate the results: process cost ($/km^3), CH_4 recovery (%) and membrane area (m^2). The units used for flow rates and compositions are km^3/day and mole %, respectively.

The first task was to determine the pressure parameters required to reproduce the results in Table 3 of the patent. By performing trial-and-error tests, the values listed in Table 1 for the feed pressure, permeate pressure and pressure drop parameters were found to provide the closet fit. In this case, the cost function had no effect because the optimal design was determined completely by the permeate composition constraint. Consequently, the results were expected to be very close if the pressure parameters were determined correctly. In fact, the optimization code produced results that were very close to those in the patent with the exception of those for a selectivity of 4.0 for which the patent results clearly violate material balance constraints. The practical implication is that the MTR membrane must have a selectivity of at least 6.5 to achieve the desired CH_4 recovery of 93%.

RESULTS AND DISCUSSION

Single Stage System

The effect of selectivity on membrane area, % CH_4 recovery and processing cost are shown in Figure 1. Increasing selectivity increases the methane recovery, but has a very small effect on membrane area, as expected. The processing cost drops over the range, but is not in the range of economic interest well beyond selectivities of 7.

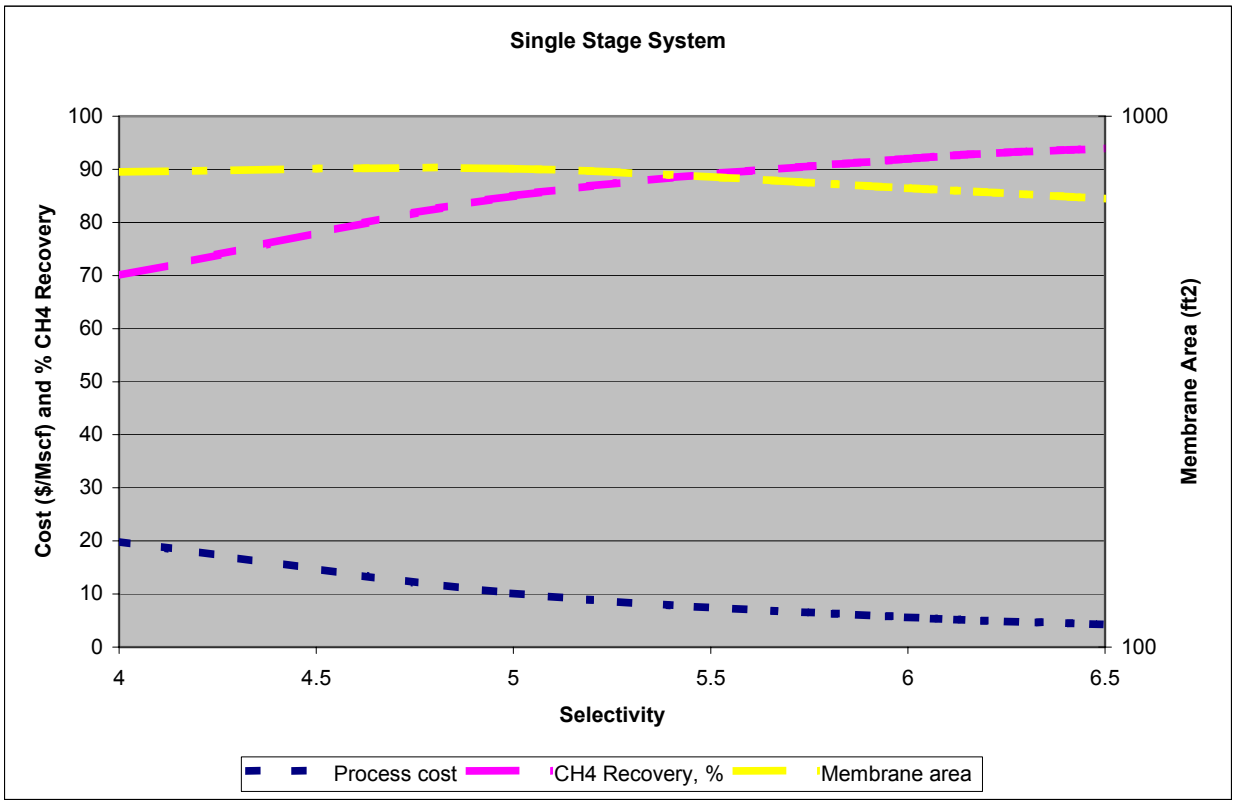

Figure 1 Effect of Selectivity for Single Stage System

The effect of nitrogen permeability on the PROPOSED membrane performance is shown in Figure 2 and Figure 3. For these figures, the permeability was varied over 5 orders of magnitude, from 10(-4) to 10(1), keeping the CH_4/N_2 selectivity to 3.0. The methane recoveries are too low because of the relatively low selectivity regardless of the value used for the N_2 permeability. The N_2 permeability has a negligible effect on economics at high values. The membrane area decreased indirectly with the permeability. Therefore, multiple stages with recycle at much higher permeability were investigated next.

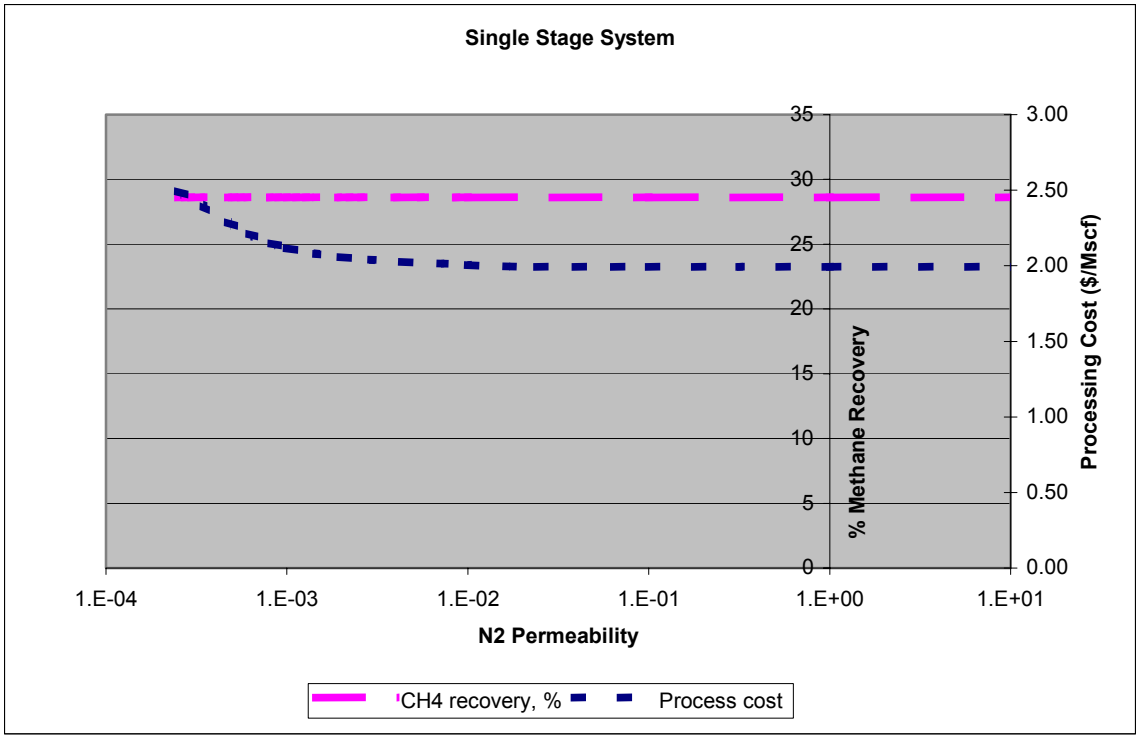

Figure 2 Effect of Permeability on Recovery and Cost

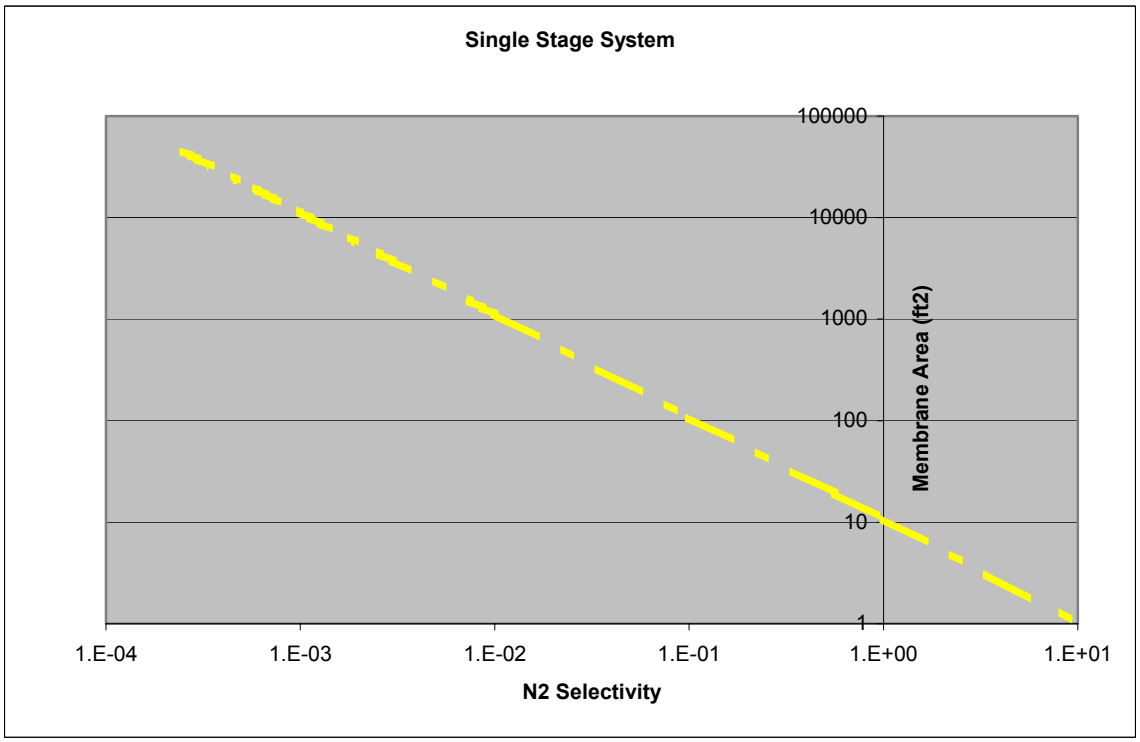

Figure 3 Effect of Permeability on Membrane Area

Multiple Stage Systems

Various two- and three-stage systems were analyzed. In multiple stage configurations, recycle and compression are used to minimize hydrocarbon loses. Figure 4 shows the effect of the different configurations on the methane recovery, membrane area and the required compression power required. Figure 5 shows the relative processing cost for each system. The figures show that the two-stage system with residual recycle had the lowest area and compression costs of the two-stage systems, while the three-stage system had the overall lowest operating cost. The estimated cost is, however, too high to be of commercial interest.

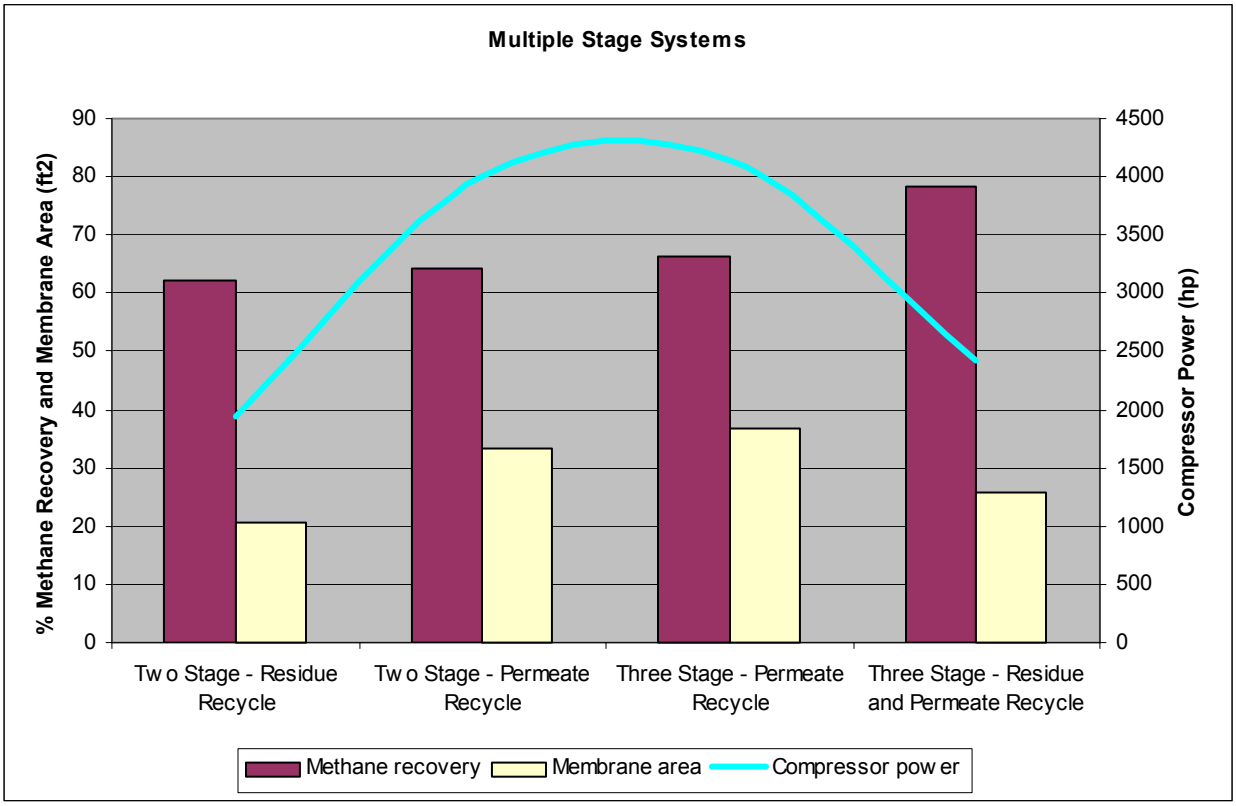

Figure 4 Membrane Area, Methane Recovery and Compression for Multiple Stage Systems

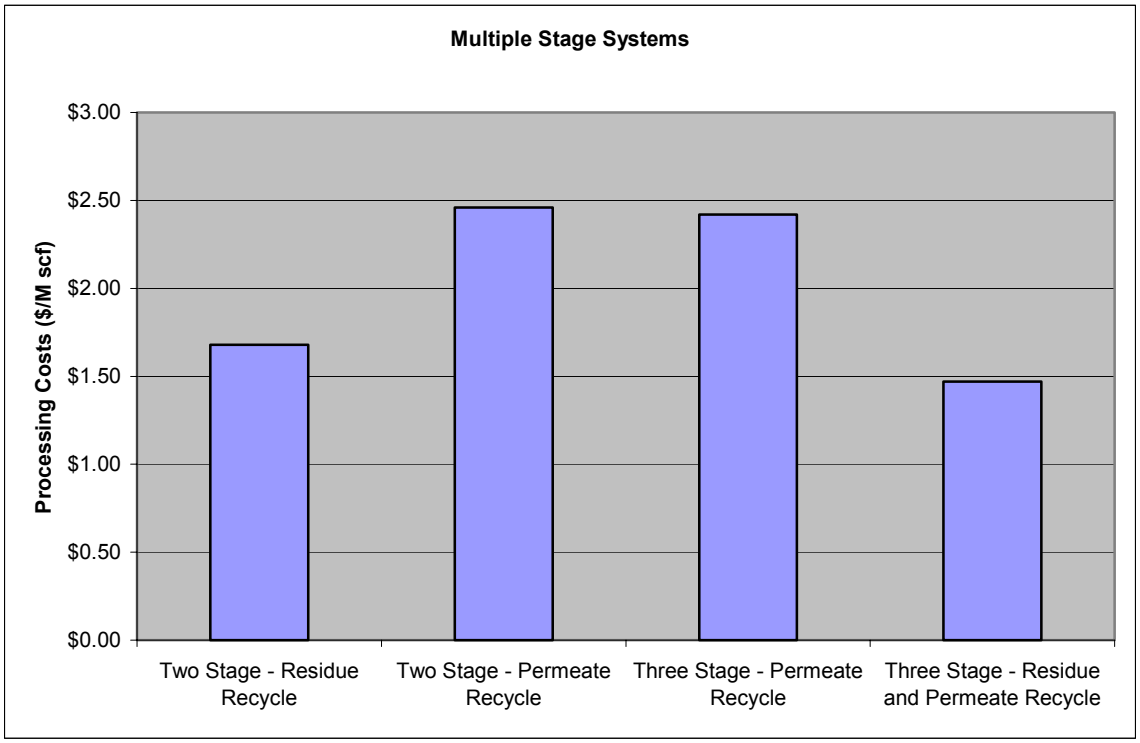

Figure 5 Processing Costs for Multiple Stage Systems

The relative economics of PROPOSED membrane were improved for feed composition of 90% CH_4 as compared to those obtained for the lower feed composition, however, the process treating cost remained very high due to low recovery and high compression costs. Extrapolating the data showed that a selectivity of greater than 5 is needed for the membrane to be competitive at a feed composition of 90% CH_4. Consequently, an increase in selectivity is required for the membrane to be economically viable. High permeability of the membrane had little impact on the overall process economics.

CONCLUSIONS

The economic potential of a highly permeable, methane-selective membrane was investigated and it was found that:

1. Unless the CH_4/N_2 selectivity can be increased from 3 to at least 5 and probably beyond 7, the proposed membrane has little commercial potential. The results indicate that the CH_4/N_2 selectivity of the proposed membrane is too low for an economic process regardless of the CH_4 permeability.
2. While the high permeability of the proposed material reduces the membrane area tremendously, the effect on overall processing costs is small.
3. Increasing amounts of nitrogen in the feed gas will require even further increases in the CH_4/N_2 selectivity for the proposed membrane to be competitive commercial technology.

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