Novel Composite Membranes and Process for Natural Gas Upgrading

Annual Progress Report - 2001

Phase I: Product Development
Phase II: Pilot Scale Demonstration

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ABSTRACT

The first phase of this project involved the development of a high performance composite membranes for the treatment of natural gas. The objective of the second phase is to demonstrate the commercial potential of a full-size membrane module in a pilot scale field test. This phase is undertaken jointly with our commercial partner, UOP LLC. At the conclusion of Phase I, two composite membrane products had been developed for the enrichment (sweetening) of natural gas. The one was a low pressure membrane with a high CO_2/CH_4 separation factor that falls within the target range of 25-30 (at 50°C) set for the program. This is a significant improvement over current commercial membranes that have separation factors of around 18-19. The second membrane had excellent high pressure capability and good contamination resistance, with a separation factor of 20-22. Based on the performance and the economic evaluation of the newly developed membranes, and with the input of UOP and DOE, it was decided to devote the demonstration phase of the program to the field testing and commercial evaluation of natural gas dehydration membranes. Due to the events of September 11, the program was also extended by 6 months until June 30, 2002. In Phase II, UOP has essentially completed preparation of the field test site. Site preparation included the re-design of the test system, purchase and installation of analytical equipment, and making the necessary piping and other hardware changes. IMS has produced two commercial sized dehydration membrane modules for the field tests. These have been successfully tested up to pressures expected in the field tests, and the modules have been shipped to the test site. The remainder of the program will comprise performance testing of the membrane modules, evaluation of the results and submission of the final report with recommendations.

TABLE OF CONTENTS

APPENDICES

INTRODUCTION

Innovative Membrane Systems, Inc., a wholly owned subsidiary of Praxair, Inc., has developed novel technologies for the manufacture of two types of composite hollow fiber membranes that can be employed for the sweetening and dehydration of natural gas. One of these membranes is a composite polyimide hollow fiber developed for the removal of carbon dioxide from natural gas, i.e. for gas sweetening. The other membrane is a composite membrane with a unique hydrophilic separation layer specifically developed for natural gas dehydration. Both of these membranes are designed and constructed to operate in a high pressure natural gas environment. Because of their simplicity and modularity, membranes are highly suited to address current natural gas processing needs.

Initially, a two year ($650,000) research program was proposed to develop and demonstrate a novel membrane platform for natural gas upgrading. The events of September 11 had a negative impact on the project schedule and the duration of the program was extended by 6 months, so that it now terminates on June 30, 2002. Phase I occupied the first 15 months of the program (2000 / 2001) and involved the development of a high performance composite membrane for carbon dioxide removal from natural gas, as part of a broad membrane platform for natural gas upgrading. Phase II is the demonstration phase of the program, where the commercial potential of the new technology is demonstrated by pilot scale field testing. This phase is undertaken jointly with our commercial partner, UOP LLC. The economic potential of the newly developed membrane technology for onshore and offshore treatment of natural gas will also be evaluated and compared to existing technologies.

At the end of the membrane development phase of the program, evaluation of the results prompted a refocus of program objectives. It was decided that potential program benefits would be maximized if the focus of Phase II was to field test a membrane system for natural gas dehydration, rather than for carbon dioxide removal. This report covers the last 3 months of Phase I and the first 9 months of Phase II.

Project Objectives and Strategy

The first program objective is to develop a novel composite hollow fiber gas separation membrane for upgrading natural gas by sweetening or dehydration, and to demonstrate a step change improvement in the economics of natural gas upgrading by this new membrane technology. The second objective was to develop a broad-based membrane technology platform that includes carbon dioxide removal and the removal of other contaminants, such as moisture, from low quality natural gas, in order to upgrade the gas to pipeline quality.

Research and Development Program (Phase I)

The new composite membrane preparation methodology developed by IMS forms the basis of the Research and Development Program. We utilize existing composite membrane manufacturing and module construction equipment, including proprietary patented hollow fiber spinning and coating equipment and computer controlled winding technology in module construction. Production scale R&D equipment includes single filament and multifilament spinning and coating lines, module construction and related testing equipment.

The initial focus of the program was to develop and demonstrate a natural gas sweetening membrane with a CO_2/CH_4 separation factor of 25 - 30 and a CO_2 permeance above 40 GPU (10^{-6} $cm^3(STP)/cm^2$ sec cmHg). Composite hollow fiber membranes with a novel polyimide separation layer were developed for this task. The work was to be extended to composite membranes with coating chemistries tailored towards natural gas dehydration and H_2S removal applications. After consultation with DOE, it was decided to focus on the development of composite membranes that are capable of operating satisfactorily at pressures above 800 psi. Both gas sweetening and dehydration membranes were developed from this technology base. Although the performance targets of this program have been met, a critical evaluation of the commercial potential of the two membrane types indicated that the field test demonstration should involve dehydration, rather than sweetening membranes.

The broad objective of this final phase of the program is to construct and test a natural gas dehydration membrane on a scale and under conditions that can be projected to commercial applications. This phase is a combined effort of IMS and UOP, where IMS will manage the project and fabricate the membrane cartridges, while UOP will conduct the field tests at their natural gas test site. Finally, the results will be evaluated on both technical and economic grounds to assess the commercial potential of the membrane for gas dehydration.

Tasks for Year 2001: Phase I

Phase I (Year 2000) involved the development of natural gas sweetening membranes. This work continued in 2001 with the following tasks for the remainder of Phase I.

Task 1. Hollow fiber membrane development

This task involved the development of a hollow fiber substrate for high temperature operation, formation of composite membranes by coating a specialized coating material onto the substrate, and integrated performance and pressure testing of composite membrane test modules using selected test gases.

Task 2. Membrane module (cartridge) development

Module development includes the modeling of flow dynamics through and around the fibers in the membrane module, and construction of modules from coated fibers. The module must also be capable of high pressure operation in a natural gas environment. During membrane formation prototype modules are constructed and continuously undergo detailed performance testing.

Task 3. Membrane response to feed stream contaminants
Membranes intended for natural gas applications are exposed to contaminants in the feed stream and their response to these contaminants must be evaluated beforehand. Membrane samples are exposed to a representative organic vapor and their permeation properties are monitored to evaluate the effect of the vapor.

Task 4. Process modeling and economic assessment
Process modeling and economic evaluation will provide targets for membrane module performance and cost that will be incorporated into product design guidelines. Targets for module performance include membrane separation factors and permeances, feed and permeate pressure and temperature, and pressure drop requirements.

Tasks for Year 2001: Phase II
Following the membrane development phase (Phase I), progress was evaluated and the following tasks were formulated for Phase II, the demonstration phase.

Task 1. Manufacture of membrane modules for field testing
This task includes design of the membrane cartridge and sizing of its components, development of a high pressure hollow fiber, and testing of the fibers for collapse pressure and separation performance. This is followed by the construction and testing of mid-sized hollow fiber modules. If performance parameters are met, scale-up continues to full-sized membrane cartridges. Membrane manufacture involves spinning and coating of hollow fibers, winding and potting the fibers to form cartridges, and quality control of the cartridges as they are produced.

Task 2. Field test site design, preparation and commissioning
This task involves the formulation of commercial performance targets, design of the test site for dehydration testing, installation of on-line analytical equipment, and modification of piping and other hardware components. This is followed by detailed safety and engineering tests before installation and performance testing of the membranes.

Task 3. Pilot plant field testing
After commissioning the test site, separation performance of the dehydration modules are monitored continuously for over a period of operation. For natural gas dehydration it is important to determine the efficiency of moisture removal, and the extent of methane loss during operation.

Task 4. Evaluation of field test results and economic assessment
The technical results of the field tests are processed and evaluated with the use of computer process models. A final evaluation combines the technical and economical aspects of the membrane separation to determine the commercial potential of the system for natural gas dehydration.

EXECUTIVE SUMMARY

Innovative Membrane Systems, Inc. (IMS) developed novel technologies for the manufacture of two types of composite hollow fiber membranes that can be employed for the sweetening and dehydration of natural gas. One of these membranes is a polyimide hollow fiber developed for the removal of carbon dioxide from natural gas, i.e. for gas sweetening. The other membrane has a unique hydrophilic coating specifically developed for natural gas dehydration.

Initially, a two year research program was proposed to develop and demonstrate a novel membrane platform for natural gas upgrading. The events of September 11 had a negative impact on the project schedule and the duration of the program was extended by 6 months, so that it now terminates on June 30, 2002. Phase I occupied the first 15 months of the program (2000 / 2001) and involved the development of a high performance composite membrane for carbon dioxide removal from natural gas, as part of a broad membrane platform for natural gas upgrading. Phase II is the demonstration phase of the program, where the commercial potential of the new technology is demonstrated by pilot scale field testing. This phase is undertaken jointly with our commercial partner, UOP LLC. At the end of Phase I, it was decided that potential program benefits would be maximized if Phase II was refocused to demonstrate natural gas dehydration, rather than for carbon dioxide removal. This report covers the last 3 months of Phase I and the first 9 months of Phase II.

The first phase of this project involved development of high performance composite membranes for carbon dioxide removal from natural gas. Hollow fiber substrates were formed with optimal dimensions for high pressure natural gas separations and for high productivity performance. Extensive experimental development led to the production of two hollow fiber substrates from different polymer materials with different pressure ratings and separation properties. The one substrate is capable of operation at intermediate pressures up to 700 psig, while the high pressure substrate operates at pressures exceeding 1,100 psig.

Membrane formation studies suggested that the processing conditions during the preparation of composite membranes appear to affect their gas transport properties. Consequently, alternative coating procedures, as well as formulations, were investigated to mitigate these effects. Initial studies were performed on dense polymer films and then extended to the formation of small scale composite membranes. In addition to pure and mixed gas performance tests with a CO_2/CH_4 feed, membrane performance was also measured in the presence of hydrocarbon compounds (contaminants) typically found in natural gas feed streams. Contaminant testing was performed to determine the durability of the membranes under actual field conditions. The results were positive and showed that the new membranes are potentially capable of operating in the presence of the contaminants typically present in natural gas applications.

The membrane development was supported by the creation of several computer models of increasing complexity to simulate natural gas separation by membranes. Initial models focused on a single stage membrane system without recycle and consider the pressure drop in both shell and bore sides. The gas mixture is treated as an ideal gas for simulating the separation of CH_4/CO_2 during natural gas processing. These membrane performance models were extended to models for process simulation and economic assessment of the new membranes. The final economic evaluation program considered a two-stage membrane cascade with recycle, and results showed that the overall separation costs of the new low pressure membrane are similar to those of existing commercial membranes. However, use of the new membrane leads to a significant reduction in the costs of energy and hydrocarbon losses which could have significant separation cost benefits in certain natural gas applications.

Preliminary scale-up to mid-sized modules was performed on the best candidate membranes. At the conclusion of the development of composite membrane modules in Phase I, two products had been developed for the enrichment of natural gas. One is a low pressure membrane with a high CO_2/CH_4 separation factor that is within the target range of 25-30 (at 50°C) set for the program. This is a significant improvement over current commercial membranes that have separation factors of around 18-19. The second membrane has excellent high pressure capability and good contamination resistance, with a separation factor of 20 - 22.

The performance results and the economic assessment of the newly developed membranes, provided a guide to the planning of Phase II, involving the field testing of IMS's commercial size natural gas dehydration membranes. This phase is undertaken jointly with a commercial partner, UOP, who will perform the pilot scale demonstration at their natural gas field test site.

UOP has essentially completed preparation of the field test site. Site preparation included the re-design of the test system, purchase and installation of analytical equipment, and making the necessary piping and other hardware changes. IMS has produced two commercial sized dehydration membrane modules for the field tests. These have been successfully tested up to natural gas feed pressures expected in the field tests. One of the membrane modules has been shipped to the test site. The remainder of the program will comprise performance testing of the membrane modules, evaluation of the results and submission of the final report with recommendations.

MEMBRANE DEVELOPMENT

The first phase of this project involved development of high performance composite membranes for natural gas sweetening (CO_2 removal). This phase extended into the first part of the 2001 project year. The results prompted the decision to proceed instead with the development of natural gas dehydration membranes for pilot scale field testing in the second program phase. This report covers those membrane developments that took place during the 2001 project year.

Composite membrane formation involves the coating of a separation layer onto a porous hollow fiber substrate. The coating material that forms the separation layer for gas sweetening is a novel precursor polymer that is cured to form a polyimide with high selectivity and good productivity (CO_2 permeation rate) for natural gas separations. The precursor is the polyamic acid salt (PAAS) form of a polyimide which is imidized by heat treated at moderate temperatures. For natural gas dehydration membranes, the coating polymer is highly permeable to water and has a low permeability to those components of natural gas that have a high calorific value, mostly the lower hydrocarbons.

Hollow fiber substrate development

Natural gas separation is typically performed at high pressure (around 1000 psi) and the pressure difference across the fiber (i.e. difference between pressure at fiber OD side and pressure at fiber ID side) can be very high. To prevent the collapse of the hollow fiber at this high-pressure differential, and to maintain the membrane productivity, the hollow fiber substrate must have both superior mechanical properties and a high porosity. In addition, the fibers must have inner and outer cross-sectional dimensions that optimize the flow and separation conditions in the membrane cartridge for natural gas dehydration. When considering the hollow fiber substrate, these properties are related to the nature of its porous structure, which is in turn determined by the hollow fiber spinning conditions.

The target fiber dimensions (fiber ID and OD) for this project were first identified, using a model for a membrane module with appropriate feed and product concentrations and expected operating conditions. The dimensions are selected so as to minimize pressure drop and maintain gas flow conditions such that the membrane module performance is optimum. Extensive fiber spinning experiments were performed with spinning dopes of various compositions, using a range of spinning conditions. A first objective was to produce hollow fibers with the target ID and OD that were substantially free of defects.

Collapse pressure of hollow fibers

To produce a hollow fiber with good pressure capability, a structural polymer with a high modulus was used to impart strength to the fiber. Collapse tests were conducted using a gas mixture of He and N_2. It was found that the collapse pressure, as related to fiber morphology, was largely dependent on the composition of the membrane casting solution (dope) and fiber ID/OD ratio. In initial fiber development, IMS produced hollow fibers with suitable dimensions and with the capability of withstanding high-pressure differentials.

A second generation of hollow fiber substrates was prepared from a new polymer more suitable for natural gas treatment. This development was based on our findings that composite membranes suffered significant permeability decline at high pressure. The decline occurred despite the fact that the fibers had satisfactory collapse pressure. The objective was to spin new fibers from a higher modulus polymer that is more resistant to compaction at elevated pressures and would operate satisfactorily in the presence of contaminants typically found in actual natural gas treatment environments. In single filament spinning experiments eleven variants of the basic fiber were produced under different spinning conditions, also utilizing different spinning solution compositions. These fibers were screened in terms of their pressure resistance and permeation properties.

Collapse pressure test results showed how the membrane performance responds to increasing pressure, and also shows when the fiber structure effectively collapses. This is the operating pressure at which a catastrophic loss of gas separation efficiency occurs. Several sets of controlled experiments showed that some of the new experimental fibers had a significantly higher collapse pressure (up to 25%) than that predicted for conventional fibers. Permeation test results showed that we were able to produce substrates with a good permeation rate and a He/N_2 separation factor typical of a fiber that would be amenable to further coating. These substrate fibers were then used to develop composite membranes as described below.

Following the successful testing of the experimental fibers, the process was scaled up to the level of commercial fibers. The fibers produced in this process were again evaluated in terms of their pressure capability and permeation characteristics. It was demonstrated that a suitable hollow fiber support can be produced on a commercial scale. These high pressure fibers were later used for the production of membranes for natural gas sweetening and or natural gas dehydration. The dehydration membrane production was scaled up to commercial size for eventual field testing.

Composite membrane development

Composite membrane formation

The hollow fiber substrate is coated with a thin layer of a selective polymer developed for the target application. Different selective layer chemistries are employed for natural gas sweetening and for dehydration applications. The polymer is dissolved in a solvent, and the solution is applied to the hollow fiber substrate by dip coating, using methods that have been optimized at IMS over many years. The result is a composite membrane with a porous fiber substrate and an ultrathin separation layer with a high selectivity for the target species: CO_2 for gas sweetening and water for dehydration.

Integrated performance testing

Extensive testing facilities enable us to measure the permeability of membranes for various natural gas components, including CH_4, CO_2, H_2O, and N_2. Separation and permeation performance can be measured at different temperatures and pressures. The feed is either pure or mixed gas, and feeds are in flow-through or dead-end mode arrangements, with provision for an inert sweep gas on the permeate side. Facilities exist for membrane modules ranging in size from a few fibers, to large commercial size cartridges. During the membrane development stages, hollow fibers are tested in small modules (8 fibers) or mid-sized modules (~80 fibers). However, IMS does not have the capability of performing field tests on commercial sized cartridges, and this facility is provided under subcontract by UOP.

Performance enhancers in the membrane coating

In the course of the project it appeared that the operational environment during the preparation of composite membranes affected their properties. Consequently we investigated changes in coating formulations that could mitigate these effects. The objective of the work was to investigate new formulations of the polyimide coating material, in order to counteract the degradation of the polymer properties during subsequent treatment and over time. Initial studies were performed on dense polymer films and then extended to the formation of small-scale composite membranes. Eventually the methodology was used to produce mid-sized membrane modules.

Substrate hollow fibers were coated with polymer containing different concentrations of a number of performance enhancing materials. Small scale modules of composite hollow fiber membranes were tested over a ten day period on a mixed gas feed of CO_2/N_2. The membrane types that we compared were two polyimide-coated composite membranes prepared for natural gas separation, one of which contained a stabilizer in its coating. Two modules of each type were prepared and tested. The first objective was to determine the stability of the membranes containing stabilizer versus those without stabilizer. A clean gas feed was passed through the membranes at test conditions of 150 psig and 50 °C.

Two of the new formulations showed an increase in CO_2 permeation rate without any significant change in selectivity. The data was incorporated into a model that projected the permeability over time. The model indicated that the permeability after one year would not change significantly. This strategy was subsequently used in the production of scaled-up membrane modules.

Extensive experimentation to study the effects of a large number of coating variables, yielded a coating methodology for composite membranes with the target properties anticipated in the program proposal. These properties are a CO_2/CH_4 separation factor of 25- 30 and a CO_2 permeance above 40 GPU. In fact, at moderate pressures, our membranes had the requisite CO_2/CH_4 separation factor and a permeance 40% higher than the target value.

Membrane response to feed stream contaminants

When membranes are intended for commercial applications it is important to determine their resistance to contaminants in the feed stream. Experience indicates that a single solvent vapor can be representative of the action of a wide range of organic contaminants typically found in commercial natural gas streams. In this task, natural gas membranes were subjected to contamination tests to determine the likely effect on their performance.

Using a model solvent, membrane samples were first stabilized under a flow of nitrogen for several days. They were then exposed to a stream of nitrogen-containing organic vapor and periodically tested *in situ* with a mixture of CO_2/CH_4 to determine the change in permeation properties. After exposure, the samples were purged with nitrogen and retested. The results of several experiments showed a moderate *initial* decrease in CO_2 permeation rate and CO_2/CH_4 selectivity, followed by a steady recovery towards pre-exposure properties after the nitrogen purge. These results were very encouraging and we concluded that the membranes sustain no permanent damage after being challenged with an aggressive organic vapor.

Membrane module development

Modeling flow dynamics
The flow dynamics in a membrane module is an important performance design parameter. Flow dynamics is influenced by the fiber packing density, hollow fiber dimensions and fiber orientation, and performance is optimum when the feed and permeate streams are countercurrent. For this program, the flow dynamics of the membrane module was reevaluated and optimized using computer models.

Cartridge / module construction
Module manufacturing procedures involve patented methods of winding and sealing the hollow fibers to form a membrane module or cartridge. Optimization of the cartridge manufacturing procedure involves selection, testing and optimizing of candidate epoxy resins to achieve the high pressure capability required of natural gas membranes in field tests. IMS has facilities for the large-scale continuous production of hollow fiber modules with a computerized system for winding the coated hollow fiber onto a core. Tubesheets are then applied to the fiber bundle to form a membrane module. In order to optimize the flow patterns within a module, winding methodology was optimized to control the packing density and orientation of fibers.

In this program, module development started with the construction and performance testing of small laboratory scale units. This was followed by modules containing an order of magnitude more fibers and culminated in mid-sized modules with several square feet of membrane area. This scale-up process enables us to determine early on whether there are any stumbling blocks to full scale module production. The module production methodology was subsequently used in the construction of the commercial size modules that are to be used in the field tests in Phase II.

Process modeling and economic assessment

Process modeling and economic evaluation provides targets for membrane module performance and cost that are incorporated into product design guidelines. Targets for module performance include membrane separation factors and permeances, feed and permeate pressure and temperature, and pressure drop requirements. Modeling is also used to determine optimum fiber dimensions required for the specific operating conditions encountered in natural gas treatment. The following three models were developed during the course of this project year.

Model 1: Cross-flow mode – single stage – no recycle

A mathematical model of natural gas separation by hollow fiber membranes has been developed. This involves formulation of the governing differential equations to describe the separation process, and establishing numerical methods to solve the differential equations and simulate the separation process. The first model is a program that simulates natural gas separation in the cross-flow mode.

Model 2: Cross-flow & Countercurrent modes – single stage – no recycle

The cross-flow mode program was then extended to a more comprehensive model that simulates natural gas separation for both cross-flow and countercurrent flow modes. This program is for a single-stage system without recycle and considers the pressure drop in both shell and bore sides. The gas mixture is treated as an ideal gas in the separation process. Subsequent work involved improving the stability of the computer program for simulating the separation of CH_4/CO_2. This program is more reliable and runs faster than its previous version.

Model 3: Two-dimensional composite membrane model

We performed a modeling study to evaluate the potential performance of a polyimide presursor coating on an alternative polymeric substrate, which is generally preferred over polysulfone for natural gas applications and also has a higher tensile modulus. The study yielded the substrate porosity that is required to produce composite membranes with a commercially acceptable permeation rate and separation factor. The results also provided guidelines for substrate development using this new polymer.

Economic analysis of Natural Gas Sweetening

Two new membranes have been developed as outlined above. One of the membranes is suitable for lower pressure applications ($\leq$ 700 psi differential) while the other membrane can be operated at up to 1100 psi. In this economic analysis, these membranes are compared to a current generation membrane for natural gas purification. While the newly developed membranes exhibit superior selectivity, their CO_2 permeabilities are not as high. Therefore, the objective of this economic assessment is to determine if the developed membranes represent economically attractive alternatives to current technology.

Performance analysis of a single stage membrane permeator yields the extent of separation attainable (concentrations of permeate and retentate streams), the required membrane area and the power or energy requirements for separation. Such an analysis depends on the following factors:

- separation properties of the membrane (separation factor and permeance);
- composition and flow rate of the feed stream;
- operating temperature;
- operating pressures on the feed and permeate sides of the membrane;
- stage cut – fraction of the feed flow collected as permeate;
- flow patterns on either side of the membrane, e.g. countercurrent, co-current, cross-flow.

In multi-stage membrane arrangements the fractions of permeate or retentate passing from one membrane to another and recycle rates are also taken into account.

An economic analysis determines the cost of separating a specified feed into its desired component streams, under a given set of operating conditions. Thus the performance analysis is used to determine the total separation cost from the capital investment and the operating costs. Capital investment is essentially the cost of the membrane module and the compressor. Operating cost includes the costs associated with capital recovery, hydrocarbon (mostly CH_4) losses, membrane replacement, compression energy, labor, maintenance and other operating expenses. Assumptions must be made regarding the life of the membrane, the life of the plant, the thermal efficiency of the compressor, labor indirect costs and percentage of time the plant is on-line. It is evident, that this combination of variables can generate a very large number of outcomes. However, to rationalize the comparison between different membranes, identical infrastructure and operating conditions are assumed. Nevertheless, certain outcomes of the model (such as the optimum stage cut) are generated by optimization of selected variables, while others (e.g. compressor power requirements and hydrocarbon losses) are influenced by the membrane properties.

A typical set of operating conditions was selected for the base case [1]. These conditions are summarized in the table below.

Operating Condition Basis

Process Parameter	*Value*
Feed Flow Rate (MMSCFD)	35
Feed Composition	10% CO_2, Balance CH_4
Product Composition	2% CO_2
Feed Pressure (psia)	700 (case A), 1100 (case B)
Permeate Pressure (psia)	20
Temperature (°C)	50

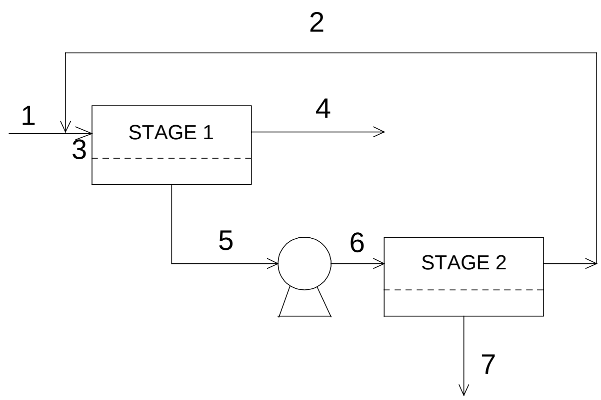
Membrane Process Configuration

It should be noted that many configurations are possible for CO_2 removal from natural gas by membranes, and that each of these configurations will impact the outcome of the analysis. The simplest case is a single permeation stage that can be operated with or without recycle. Either the permeate or the retentate can be recycled. At the next level of analysis, two membrane permeation stages can be utilized in any of the following different configurations:

- two permeation stages in series with permeate recycle;
- two permeation stages in series with retentate recycle;
- two permeation stages in cascade arrangement with permeate recycle;
- two permeation stages in cascade arrangement with retentate recycle.

The economic implications of employing each of these configurations are analyzed in depth by Bhide and Stern [1].

For the first level of economic assessment we adopted a single permeation stage configuration. This analysis was followed by a more advanced study involving two permeation stages in cascade with recycle of the second stage retentate to the feed stream. This configuration is illustrated in the following figure, which shows that the permeate from the first stage is used as feed to the second stage and the retentate from the second stage is recycled and mixed with the feed of the first stage. An earlier analysis of several potential membrane staging and recycling configurations concluded that this configuration was the most economical for the approximate conditions of this study [1].



Process scheme for two cascaded membrane units with retentate recycle

Since the single stage membrane process analysis was an intermediate step in the development of the more comprehensive economic analysis, the results are not discussed here. The evaluation of the two-stage membrane process was performed using a computer model for the prediction of hollow fiber gas separation performance. The model is based on the countercurrent flow arrangement and accounts for pressure losses on the bore (permeate) side of the membrane. Listed below, are the parameters of the model.

Total Capital Investment

- Membrane module cost
- Membrane area/shell
- Module skid cost
- Installed compressor cost
- Base plant cost
- Project contingency
- *Total Capital Investment*

Annual Variable Operating and Maintenance Cost

- Capital recovery cost
- Membrane replacement cost
- Utility cost
- Labor cost
- Operator time
- *Total labor cost*
- Contract and maintenance cost
- Hydrocarbon losses
- Total variable operating and maintenance cost

Total Gas Processing Cost

- Capital recovery cost
- Gas processing cost

The gas processing costs for the *low* pressure membrane and the current membrane technology are very similar (within 3% of each other). However, the new membrane developed in this program has about 18% lower energy and hydrocarbon loss costs. This is due largely to the better separation performance of the new membranes. The energy costs are related to compression of the feed, and are also lower for the new membrane than for the commercial membrane. In certain separation schemes this category of cost could dominate the economic comparison.

This cost advantage of reducing hydrocarbon losses and energy costs, is offset by the lower capital cost of the current state of the art membrane. Higher hydrocarbon or energy costs, or lower membrane area unit costs than assumed in this study will shift the total gas processing cost advantage towards the new membrane.

In the case of the *high* pressure membrane, there appears to be no overall economic advantage compared to the conventional membrane. The higher capital cost associated with the new membrane is not nearly offset by its lower energy and hydrocarbon loss costs. Unless the permeability of the new membrane can be significantly increased from its present value, it is unlikely to be competitive.

The conclusions of this economic study were discussed with our commercial partner, UOP, to gain input from a commercial perspective. Their feedback is discussed below.

Scale up of composite membranes

Composite membranes were taken through several stages in the scale up process. Rapid screening of large numbers of process variants was conducted on modules that contain only a few of fibers. The next stage was to produce and pot mid-sized modules that contain many hundreds of fibers. The final stage involved production of a full size module that can be evaluated in a pilot test unit. The mid-sized module represents the largest modules produced during the development phase of the project, and enabled us to decide whether or not pilot scale testing is feasible.

Mid-sized modules were produced from the two most promising of the composite membrane variants, after-treatment to cure the polyimide precursor coating. The modules were tested to determine their separation efficiency. This was done to evaluate the performance properties of the new membranes against those of commercial membranes. The results did not suggest any technical limitation to the production of commercial scale modules with gas separation properties suitable for natural gas treatment.

At the conclusion of the development of composite membrane modules in Phase I, two products had been developed for the enrichment of natural gas. The one was a low pressure membrane with a high CO_2/CH_4 separation factor that falls within the target range of 25-30 (at 50°C) set for the program. This is a significant improvement over current commercial membranes that have separation factors of around 18-19. The second membrane had excellent high pressure capability and good contamination resistance, with a separation factor ranging from 20 - 22. To decide on the appropriate membrane for the demonstration phase of the program, both the technical performance results and the economic assessment of the newly developed membranes had to be considered. The objective of the pilot scale evaluation is to verify the commercial potential of a promising product, and we were committed to carrying out the evaluation only if it would lead to meaningful conclusions.

We approached our commercial partner, UOP, for an evaluation of the new membranes in the light of their extensive commercial experience with natural gas treatment. They are also scheduled to conduct the pilot scale field tests in Phase II of the program. In its feedback, UOP acknowledged that the low pressure membranes have technical merit, but they were of the opinion that the small market size for such a niche product did not justify pilot scale field testing. However, they proposed an alternative membrane application that would merit pilot scale evaluation under this program, namely to *dehydrate* natural gas to pipe line specifications. There is a growing need for an improved technology to treat and dehydrate on-shore and off-shore natural gas, and UOP recommended that the funds and facilities for field testing be used to evaluate IMS's membranes that are specifically designed for natural gas dehydration. After consideration of the request, DOE agreed to the change in strategy and the final program phase proceeded with the objective of demonstrating natural gas dehydration in a field test situation.

PILOT SCALE FIELD DEMONSTRATION

The objective of the demonstration phase of the program is to field test a natural gas dehydration membrane on a scale and under conditions that can be projected to commercial applications. This phase is a combined effort of IMS and its commercial partner, UOP. In this phase, IMS manages the overall project and fabricates the membrane cartridges, while UOP conducts the field tests at its natural gas field test site. Evaluation of the results will be carried out jointly by IMS and UOP, while IMS is responsible for the final report.

The demonstration phase involves four tasks. The first task of designing and fabricating commercial sized membrane cartridges is executed in tandem with the second task of preparing the field test site. The remaining two tasks are to perform the field tests, and finally to evaluate the membrane performance from both a technical and an economical perspective. A detailed schedule was drawn up by IMS and UOP defining the various action items in terms of the project time line. The first two tasks essentially occupied the remainder of 2001, and details are provided below.

Progress on these tasks was on schedule, until the events of September 11 led to a temporary prohibition on travel in both UOP and IMS, and severely slowed the delivery of equipment and services to the test site. After consultation with the DOE project manager, an application was granted to postpone the project completion deadline by 6 months until June 30, 2002. All tasks in the Phase II schedule were adjusted accordingly. Current status is that all tasks are on schedule and that field testing will start in February, 2002.

Production of membrane modules

Production strategy

On the part of IMS, the first task was to determine the configuration of the membrane cartridge and size all of its components, manufacture hollow fiber dehydration membranes, and then evaluate the fibers in terms of collapse pressure and separation performance. This is scaled up to the construction and testing of mid-sized modules. If performance parameters for these modules are met, then scale up continues to the production of full-sized membrane cartridges that will be used in the field tests. It should be emphasized that these are novel membranes developed specifically for this project, and the scale-up process is necessary to reduce the risk of membrane failure during the field tests.

Membrane fabrication involves spinning and coating of specialized high pressure hollow fibers, winding and potting the fibers to form cartridges, and testing of the assembled membrane cartridges as they are produced. Only when the cartridges have met all internal quality control specifications, are they shipped to the field test site.

Hollow fiber module production

The design of the commercial size cartridge for the field test shell was completed, and detailed engineering drawings of the cartridge were prepared. These drawings were forwarded to UOP, so that complementary modifications could be made to the membrane skid at the field test site.

Based on the hollow fiber design specifications, sufficient fiber was spun and coated to produce two commercial size cartridges. A second variant of the fiber, utilizing different polymer materials was also developed for testing. The coated composite membranes were qualified at IMS by constructing a number of mid-sized test modules. These met the minimum the pressure and performance requirements, and it was decided to commence manufacture of commercial scale membrane modules for the field tests.

The composite hollow fiber dehydration membranes, comprise a pressure resistant hollow fiber substrate coated with a specialized polymer for natural gas dehydration. These hollow fiber membranes have been specifically developed for high pressure natural gas dehydration and underwent quality control tests (including pressure testing) at IMS, prior to being shipped to the field test site. Complete dehydration performance tests cannot be carried out at IMS, and these will be performed by UOP at the pilot test site.

Two commercial-sized membrane dehydration modules were manufactured at IMS, and both passed their initial quality control tests. Discussions with UOP indicated that actual test pressures at the test site might be higher than initially anticipated, and it was decided to test the membranes at higher pressures before shipping them to the site. Both of the modules have now successfully been tested up to a pressure that exceeds the expected operational pressure at the pilot test facility. The membrane modules are now ready, and one module was recently shipped to the field test site.

Field test site preparation

UOP is responsible for designing the pilot test system for dehydration testing and preparing the site for the field tests. The pilot test system forms part of a larger natural gas treatment facility, and testing procedures, as well as the feed and product gas quality, must be integrated with the requirements of the main facility. Thus, the dehydrated gas from the pilot test unit will be post-treated to pipeline quality, so that it can be returned to the main system. Similarly, the impact of potential failure of any part of the pilot test system on the main facility must be carefully considered. Site preparation involved redesign of the test system, purchase and installation of analytical equipment, and completion of the necessary piping and other hardware changes.

UOP has also completed an engineering safety review of the test site, and is addressing the issues that have been identified. These relate to the feed pressure, permeate pressure, and humidification of the gas feed to the dehydration membrane. The potential range of operating temperatures at the site are expected to vary during the course of the pilot testing. This has required that special attention be given to the design of the natural gas feed system to the membrane to ensure that the required dewpoint of the feed and product streams can be maintained and accurately measured. Critical issues here are to maintain the desired degree of saturation of the feed gas, and to minimize the risk of condensing moisture inside the membrane.

A test run of the system is also scheduled before performance testing of the commercial-sized membrane cartridges commences in February 2002.

CONCLUSIONS

Scale up of composite membranes

Composite gas sweetening membranes were successfully scaled up to mid-size modules. No significant obstacles were encountered to the eventual production of full commercial scale modules that can be evaluated in a pilot test system. The permeation test results of the mid-sized modules showed gas separation properties in the range of commercial membranes.

Phase I membrane development

At the conclusion of the development of composite membrane modules in Phase I, two products had been developed for the enrichment of natural gas. One is a low pressure membrane with a high CO_2/CH_4 separation factor that is within the target range of 25-30 (at 50°C) set for the program. This is a significant improvement over current commercial membranes that have separation factors of around 18-19. The second membrane has excellent high pressure capability and good contamination resistance, with a separation factor of 20 - 22.

Resistance to feed stream contaminants

The response of membranes to likely contaminants in the feed stream, has shown that there is a moderate *initial* decrease in CO_2 permeation rate and CO_2/CH_4 selectivity upon contact with a standard contaminant. This was followed by a steady recovery towards pre-exposure properties after purging the system with nitrogen. The membranes showed no permanent damage as a result of the challenge with the aggressive organic vapor.

Phase II objective and schedule

Based on the performance and the economic evaluation of the membranes developed in Phase I, and with the input of UOP and DOE, it was concluded that the demonstration phase of the program should focus on the field testing and commercial evaluation of natural gas dehydration membranes.

Production of membrane modules

Following scale-up from mid-sized modules, two commercial-sized membrane dehydration modules were manufactured at IMS, and both have passed their quality control tests. The modules have been tested up to a pressure that exceeds the expected operational pressure at the pilot test facility. The membrane modules are now ready for shipment to the test site where their dehydration properties will be evaluated.

Preparation of field test site

UOP is responsible for designing the pilot test system for dehydration testing and preparing the site for the field tests. Site preparation involved the re-design of the test system, the purchase and installation of analytical equipment, and making the necessary piping and other hardware changes. An engineering safety review was completed, and the natural gas feed system has been modified to maintain and measure the required dewpoint of the feed and product streams. Site preparation is on schedule, and performance testing of the commercial-sized membrane cartridges is scheduled to begin in February 2002.

REFERENCE

1. B.D. Bhide and S.A. Stern, (1993) "Membrane Processes for the Removal of Acid Gases From Natural Gas. I. Process Configurations and Optimization of Operating Conditions," *J. Membr. Sci.* 81 209-237.