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Low-Quality Natural Gas Sulfur Removal/Recovery With Membranes

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OBJECTIVES

The main objective of this program is to develop a membrane process for the separation of hydrogen sulfide and other impurities (carbon dioxide and water vapor) from low-quality natural gas. The overall program involves development and parametric testing of appropriate membrane materials in the form of thin-film composite membranes. These membranes will then be made on a larger scale and incorporated into modules which will be tested first in the laboratory, and then at different field sites. A technical and economic analysis of the membrane process will then be performed and compared with existing processes.

BACKGROUND INFORMATION

The natural gas production in the lower-48 states is expected to increase significantly in order to meet the rising demand. Natural gas supply is projected to increase by 25% between 1991 and 2010 with 70% of the increased production after 1995 coming from the Lower-48 gas fields⁽¹⁾. Recent studies of U.S. natural gas reserves have shown that an increasing fraction of the gas produced will be from smaller gas fields at remote locations, and will be sub-quality on hydrogen sulfide, carbon dioxide, and nitrogen specifications. More than 13% of current reserves are known to be contaminated with hydrogen sulfide⁽²⁾. When these subquality reserves are brought into production, new treatment facilities will have to be installed, and it is projected that between \$30-40 million will be invested every year⁽³⁾. Alternatives to currently available absorption based technologies are being sought for processing gas streams to pipeline specifications in an environmentally and economically acceptable manner.

Conventional amine processes are energy-intensive and, being complex, they require constant supervision and maintenance. They are especially prone to problems such as corrosion in the reboiler, foaming and solvent losses in the absorption column. Also, spent amines have increasingly to be disposed as hazardous wastes, which increases operating costs significantly. Membrane processes are simple and modular, offer greater operational reliability and lower maintenance costs. Membrane processes require almost no operator supervision, and, therefore, are ideally suited for operation in remote locations. Membrane processes would be very cost-competitive with conventional amine processes, especially for gas streams that contain high amounts of acid gases at low flow rates.

PROJECT DESCRIPTION

In Phase I of the program, an extensive experimental study has been performed to assess the performance of our membranes under various feed conditions. Composite membranes made from four different polymers were investigated to determine their hydrogen sulfide/methane and carbon dioxide/methane selectivity. Two polymers were then selected for a further parametric study. Effects of the following variables were studied: the feed compositions of hydrogen sulfide and carbon dioxide, the presence of water vapor in the feed

gas, and the feed gas temperature. Experiments were performed at pressures in the range 400-1,000 psig. Also as part of the Phase I evaluation, Hoechst Celanese Corporation will perform a complete economic analysis for the removal and recovery of a 1 Ton sulphur/day plant. In Phase II of the program, a bench-scale system will be constructed and long term tests will be performed. Also, this skid-mounted system will then be field-tested at one or more different field sites..

RESULTS

The following gas mixtures were used to test the membranes to understand the effect of varying the feed composition on membrane selectivity.

Table 1. Feed Gas Compositions Used in Parametric Testing.

Feed gas composition (vol%)		
H ₂ S	CO ₂	CH ₄
0.000	4.00	96.00
0.097	0.00	99.90
0.081	3.92	95.99
0.986	4.12	94.90
1.830	10.80	87.34
0.095	8.14	91.77

Experiments were performed at 400, 600 and 970 psig feed pressure, using membrane stamps with exposed area of about 36 cm². All experiments were performed at very low (< 1%) stage cut. The following important observations could be made from the experimental data obtained.

1. In general, the pressure-normalized fluxes of hydrogen sulfide and carbon dioxide decrease with increasing feed pressure, whereas those of methane increase. The decrease in the hydrogen sulfide and carbon dioxide fluxes can be explained by competitive sorption of these components in the polymer. As the feed pressure increases, both hydrogen sulfide and carbon dioxide molecules compete for the fixed number of sorption sites in the polymer. This results in a lower solubility coefficient (the ratio of the concentration in the polymer to the partial pressure) for each component. At the same time, the polymer swells, resulting in a higher diffusivity for all components, including methane. The net result is an increase in the methane flux and a decrease in the fluxes of the acid gases (hydrogen sulfide and carbon dioxide).

2. Typically, for all ternary mixtures, the hydrogen sulfide/methane selectivity is between 70 and 50 for MTR 701 and between 60 and 40 for MTR 704 in the pressure range from 400 to 1000 psig. In the same pressure range, the carbon dioxide/methane selectivity is between 16 and 14. The hydrogen sulfide/methane selectivity of the MTR 701 polymer is about three times higher than that of cellulose acetate, which is presently being used for acid gas separation. However, the carbon dioxide/methane selectivity is somewhat lower than that of cellulose acetate.

Figures 1a and 1b shows the effect of the combined partial pressures of the acid gases in the feed mixture on the pressure-normalized fluxes of all the three components in the feed. The figure shows that the pressure-normalized flux of hydrogen sulfide decreases slightly with increased acid gas partial pressure, whereas that of carbon dioxide is almost constant. The methane flux, on the other hand, increases slightly with an increase in the acid gas partial pressure.

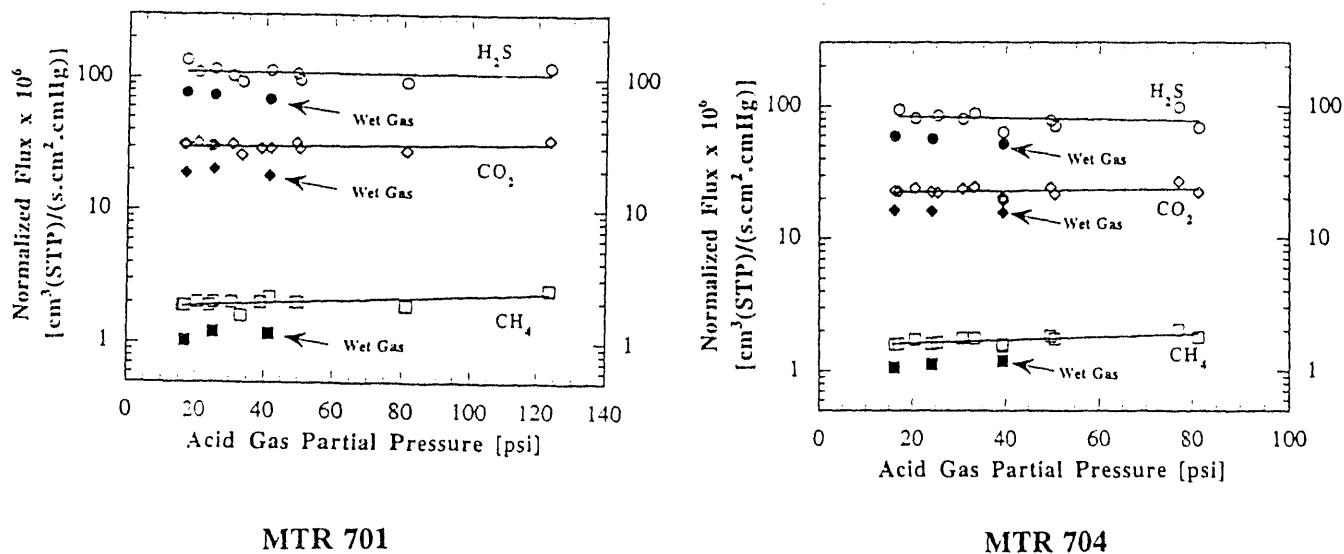


Figure 1. Pressure-normalized permeation flux of each component of the feed mixture as a function of the total acid gas partial pressure. Solid symbols represent data obtained when the feed gas was saturated with water vapor.

Figure 2 shows the effect of the acid gas partial pressure on the membrane selectivity for hydrogen sulfide and carbon dioxide over methane. This figure shows that both the hydrogen sulfide/methane and carbon dioxide/methane selectivities decrease with increasing acid gas partial pressure. At higher partial pressures, the selectivities appear to flatten out; for hydrogen sulfide/methane to about 50, and for carbon dioxide/methane to about 14.

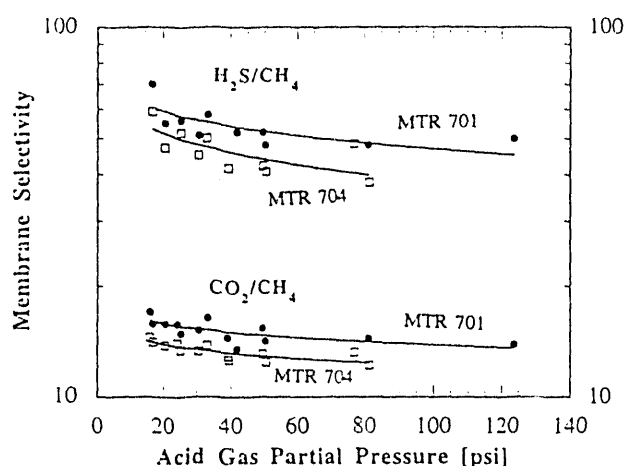


Figure 2. Selectivity for hydrogen sulfide and carbon dioxide over methane as a function of the total acid gas partial pressure in the two membrane investigated. The solid symbols represent data obtained when the feed gas was saturated with water vapor.

Figures 1 and 2 include data points that show the effect of saturating the feed gas with water vapor on the pressure-normalized fluxes and the membrane selectivities. In Figures 1a and 1b, the solid symbols represent the fluxes of each of the components through the membrane obtained with a water-vapor-saturated feed. These fluxes are lower than those obtained in the absence of water vapor. The pressure-normalized hydrogen sulfide and carbon dioxide fluxes were about 25% lower, and the methane fluxes were about 35% lower. Water, which is a strongly hydrogen-bonding molecule, is strongly sorbed by the polymer. The presence of water vapor in the polymer matrix can affect the permeation properties in two ways. Water molecules will displace both hydrogen sulfide and carbon dioxide from active sorption sites in the polymer. Also, by forming inter-chain hydrogen bonds, water vapor can restrict chain motion to some extent, and thereby decrease the diffusivity of other components. Both or any one of these effects would result in lower permeation fluxes for hydrogen sulfide, carbon dioxide, and methane in the membrane. However, this flux decrease is completely reversible, and upon changing to a dry gas, the original fluxes were obtained again.

The solid symbols in Figure 2 show the effect of the presence of water vapor in the feed on the membrane selectivity. Neither the hydrogen sulfide/methane nor the carbon dioxide/methane selectivities change significantly. In comparison, a water saturated feed can irreversibly decrease the permeation flux of hydrogen sulfide and carbon dioxide in commercially available cellulose acetate membrane due to compaction resulting in a significantly loss of separation performance.

The effect of feed temperature on the pressure-normalized permeation flux of each of the three components in the feed gas, and on the membrane selectivity was also investigated. With increasing temperature, the permeation flux of each of the three components increases, indicating an endothermic permeation process. The highest increase in the permeation flux

was for methane. This results in a lower membrane selectivity for hydrogen sulfide and carbon dioxide over methane at higher temperatures. The H_2S/CH_4 selectivity at a feed pressure of about 400 psig decreases from about 70 at 22°C to about 52 at 40°C.

In synopsis, the parametric study showed that the membranes exhibit a hydrogen sulfide/methane selectivity in the range 40-70 and carbon dioxide/methane selectivity in the range 14-16. These selectivities are maintained at pressures as high as 1,000 psig and with water vapor present in the feed gas. The methane flux of our membranes is comparable or higher than that of commercially available cellulose acetate membranes, whereas the hydrogen sulfide/methane selectivity of our membranes is two to three times higher.

We have been able to classify the opportunities for membrane processes in this area into two categories. The first opportunity exists in new gas fields or new acid treatment plants. The other opportunity is in de-bottlenecking existing amine treatment facilities, in order to either increase their gas treatment capacity, or in adjusting the feed composition in order to achieve pipeline specifications. In each of these two applications, it will be necessary to obtain a hydrogen sulfide enriched stream in an appropriate concentration range to be treated by either a Redox process, or by a Claus process for permanent fixation of sulfur. We are presently investigating the following membrane process configurations in order to achieve this objective.

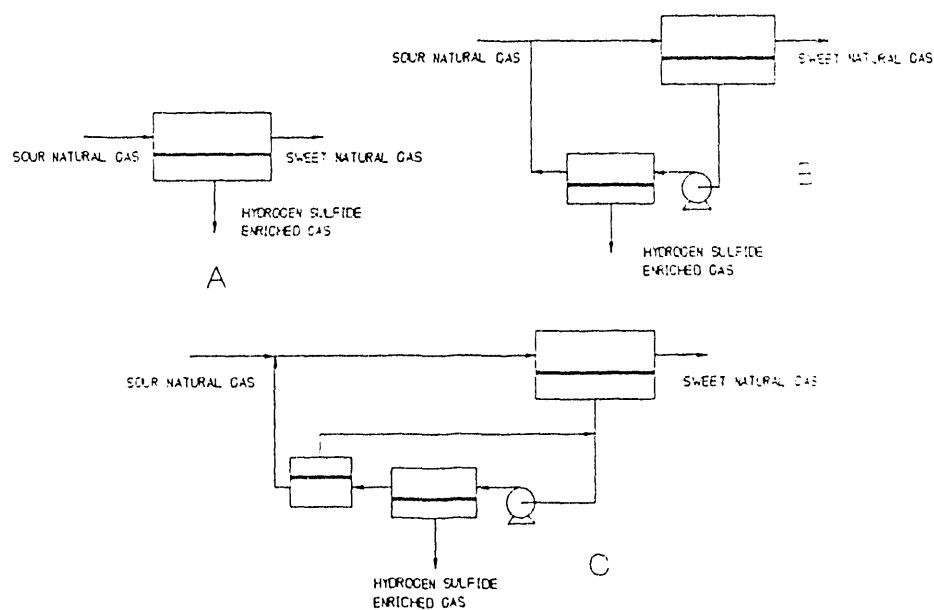


Figure 3. Membrane process configurations being studied for hydrogen sulfide separation from natural gas.

FUTURE WORK

We are presently scaling up the production of these membranes on our commercial coating machine. After optimizing the scale-up, we will incorporate membranes in spiral-wound modules. These modules will be tested by MTR using a high-pressure module test system, which has been designed for complete recycle operation. If the test results are acceptable, the modules will be tested for longer periods of time in a bench test. Hoechst Celanese Corporation will build and operate the skid-mounted field test system.

In further work, optimized designs for three of the most promising membrane applications will be developed. The technical and economic aspects of the processes will be compared to existing alternatives. After selecting the best application from the above, a complete conceptual design, including sulfur recovery and any other treatment to be combined with the membrane separation process will be prepared.

In Phase II of the program, MTR and Hoechst Celanese Corporation will build a bench-scale unit to further test the membrane modules for extended periods of time. The bench-scale unit will be skid-mounted such that it can be later transported to one or more field-sites where additional tests will be conducted on real-life natural gas streams. Upon conclusion of the field tests, a revised technical and economic analysis will be performed for the membrane process.

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