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Authors:

Stern, S.A. (Syracuse University)
Meyer, H.S. (Gas Research Institute)
Venkataraman, V.K. (DOE/METC)
Shoemaker, H.D. (DOE/METC)

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Upgrading of Raw Natural Gas Using High-Performance Polymer Membranes

**S. A. Stern, Syracuse University
Syracuse, New York**

**H. S. Meyer, Gas Research Institute
Chicago, Illinois**

**V. K. Venkataraman and H. D. Shoemaker,
U. S. Department of Energy,
Morgantown Energy Technology Center
Morgantown, West Virginia**

The separation of CO₂ and H₂S from raw natural gas is essential for enhancing the heating value of the gas and for providing environmental safety during transportation and use. Membrane separation processes are particularly useful for this application because they are inherently energy-efficient. Membrane processes also offer other important advantages, such as ease of scale-up due to module design, good space and weight efficiency and great flexibility in handling variations in the flow rate, pressure and composition of the raw natural gas streams. In a coordinated effort, the Gas Research Institute and the Department of Energy, Morgantown Energy Technology Center are funding an extensive study at Syracuse University on the relationships between the chemical structure of various polymers and their permeability to different gases. Based on criteria derived from this study, novel fluorine-containing polyimides that exhibit very high CO₂/CH₄ selectivities as well as significant H₂S/CH₄ selectivities were synthesized. These "dense" (homogeneous) membranes separated various mixtures of CO₂/CH₄ and H₂S/CH₄/CO₂ at 35°C (95°F) and at pressures up to 10 atm (147 psi). The results of these measurements agree well with computer simulations. The CO₂ content of CH₄/CO₂ mixtures containing as much as 40 mole percent CO₂ can be reduced with the polyimide membranes to pipeline specifications (≤ 2 mole percent CO₂). To reduce the H₂S content of H₂S/CH₄/CO₂ mixtures to pipeline specifications (≤ 4 ppm H₂S), the membranes are best combined with conventional gas-absorption processes, such as a selective amine. Such "hybrid" processes for the upgrading of natural gas can be more economical than conventional gas-absorption processes alone.

Natural gas is a mixture of hydrocarbon and non-hydrocarbon gases. The well head composition of these gases varies greatly across the United States. To ensure that the natural gas consumer receives a consistent, safe product, most of the gas undergoes some degree of processing to meet "pipeline" specifications. This requires the removal of the following components from the light hydrocarbon fraction:

- carbon dioxide (CO₂), which is corrosive if wet and reduces the heating value;
- hydrogen sulfide (H₂S), which is corrosive and toxic;
- nitrogen (N₂), which is inert and reduces the heating value;

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- natural gas liquids (NGL), which are valuable by-products that can cause operational problems if they condense in the pipeline;
- water (H_2O), which forms hydrates and promotes corrosion; and
- other trace constituents that may be limited by contracts or good engineering practices (including oxygen (O_2), helium (He), oils and grease, other sulfur species).

The objective of the research programs is to evaluate the potential usefulness of membrane separation processes for the removal of acid gases (CO_2 and H_2S) from *low-quality* natural gas. The maximum pipeline specifications for CO_2 and H_2S are typically 2 mole-percent and 4 ppm (volume), respectively. Across the U.S., 28.2 trillion cubic feet (Tcf) (or 20%) of the currently producing raw reserves contain greater than 2% CO_2 , while, in the future, 185 Tcf (or 83%) of the new discoveries are expected to exceed the CO_2 specification. Similarly, 19 Tcf of currently producing reserves and 77 Tcf of new discoveries are expected to exceed the H_2S specification.

Commercially, there are four general types of processes used to removed these acid gases from natural gas, namely:

- reversible chemical or physical absorption into a liquid solvent;
- direct conversion through absorption and oxidation in a liquid;
- adsorption on a solid; and
- physical separation through a permeable membrane.

The primary means used commercially is the chemical solvent. In those systems, an amine solution is circulated between an absorption and regeneration tower. In the absorber, the amine flows counter-current to the flow of the high pressure, raw gas. The acid gases chemically react with the basic solution. The solution, now rich in acid gases, is pumped to a low pressure, high temperature regenerator to reverse the absorption reaction. The lean amine is cooled and returned to the absorber. The acid gas stream is treated further as required to handle the CO_2 and/or H_2S streams.

Membrane separation units offer several process advantages that make them attractive for acid gas removal from natural gas. Within the basic unit itself, there are no moving parts, membrane units can be easily replaced, variations in flow rates can be easily accommodated and startup can be accomplished in a very short time. In addition, the available information suggests that the operation of a membrane process may require less labor than other process options. However, current membrane performance and fabrication technology may limit the use of this technology to relatively small-scale applications because of the modularity of the separation units. Other separations technologies, because of favorable economies of scale, will be more attractive at larger scale. The crossover between membranes and amines is dependent on the concentration of CO_2 and H_2O content of the gas, as well as site specific issues, but in a study conducted for the Gas Research Institute (GRI), M.W. Kellogg found that the crossover may be about 30-75 million standard cubic feet per day (MMscf/d) with the current generation of membranes.

GRI and the Department of Energy, Morgantown Energy Technology Center (DOE-METC) have initiated programs to develop new membranes for natural gas separations that offer the potential to reduce processing costs and expand the arena of applicability to larger-scale operations. New types of polymer membranes that exhibit high gas selectivities are being tested for this purpose by Syracuse University. This project is comprised of gas permeability and separation measurements, process design studies and economic evaluations.

A laboratory-scale apparatus of the "time-lag" type was constructed for this project. The apparatus is being used for both (1) gas permeability and selectivity measurements and (2) gas separation measurements. The first types of measurements are being made at very low "stage cuts" (<0.001) to determine the permeability coefficients of the components of CH_4/CO_2 and $\text{CH}_4/\text{CO}_2/\text{H}_2\text{S}$ mixtures, as well as the CO_2/CH_4 and $\text{H}_2\text{S}/\text{CH}_4$ selectivities of the membranes. (The stage cut is the fraction of the feed permeating through a membrane.) Values of the permeability coefficients are required for computer simulations of membrane processes for the removal of CO_2 and H_2S from low-quality natural gas. The gas separation measurements are being made at higher stage cuts to validate the results of the computer simulations.

Four new types of polymers synthesized at Syracuse University were evaluated for possible use as membrane materials for the upgrading of low-quality natural gas. Three of these polymers, D-2, E-1 and F-1, were polyimides; the fourth polymer, G-1, was a polypyrrolone. The D-2 and G-1 polymers contain fluorine atoms in their repeat units, whereas E-1 and F-1 do not. The permeability measurements were made at 95 °F (35 °C) with binary CH_4/CO_2 gas mixtures containing 10, 20, 30, and 40 mole-percent CO_2 , and with a ternary gas mixture of 87.5 mole-percent CH_4 , 9.7 mole-percent CO_2 , and 2.8 mole-percent H_2S . The feed ("upstream") pressure was varied in the range from about 59 to 200 psia (4 to 13.6 atm), whereas the permeate ("downstream") pressure was 0.005 to 0.58 psia (0.3 to 30 torr). The polymers were used in the form of "dense" (homogeneous) membranes.

The CO_2/CH_4 selectivity of the polymers studied, at 95 °F (35 °C) and at 147 psia (10 atm), was found to decrease in the following polymer order when measured with a binary CH_4/CO_2 gas mixture:

CO_2/CH_4 Selectivity Order

Polymer	D-2 >	F-1 >	G-1 >	E-1
Feed Gas @ 10% CO_2	85	52	45	39
Feed Gas @ 40% CO_2	60	40	35	26

The CO_2/CH_4 selectivity decreases with increasing CO_2 concentration in the feed mixture, suggesting that the polymers were plasticized (swelled) by CO_2 , as has been reported for many

other glassy polymers, as shown in Figure 1 for polymer D-2. The decrease in the CO_2/CH_4 selectivity with increasing CO_2 concentration was due mainly to an increase in the CH_4 permeability; by contrast, the CO_2 permeability remained essentially unchanged. This behavior is because CO_2 exhibits a much higher solubility in the polymers than CH_4 . Consequently, CO_2 plasticizes the polymers to a much greater extent than CH_4 , and thereby increases their permeability to CH_4 .

As typically shown in Figure 1 for polymer D-2, the CO_2/CH_4 selectivities of the D-2, G-1 and F-1 polymers are not significantly affected by an increase in the total "upstream" pressure in the range from 59 to 200 psia. The effect of upstream pressure on polymer E-1 has not yet been studied.

The CO_2 permeability of the polymers, at 95 °F (35 °C), 147 psia (10 atm) when measured with a binary gas mixture containing 10 mole-percent CO_2 , decreased in the following polymer order:

Figure 1. CO_2/CH_4 Selectivity of Polyimide D-2 is fairly constant with total applied pressure.

Polymer	G-1 >	D-2 >	F-1 ≈	E-1
CO_2 Permeability $\times 10^{10}$	29.2	7.25	1.96	1.65

where the permeability coefficient for CO_2 is given in units of $\text{cm}^3(\text{STP})\cdot\text{cm}/\text{s}\cdot\text{cm}^2\cdot\text{cm}\cdot\text{cmHg}$. It is seen that the CO_2 permeability does not decrease in inverse polymer order with increasing CO_2/CH_4 selectivity.

The extent of separation achieved with D-2 polyimide membranes was measured as a function of the stage cut, as shown in Figure 2. The measurements were made at 95 °F (35 °C) at 147 psia (10 atm) using two feed mixtures: a 90/10 mixture of CH_4/CO_2 and a ternary 87.5/9.7/2.8 mixture of $\text{CH}_4/\text{CO}_2/\text{H}_2\text{S}$. The CO_2/CH_4 and $\text{H}_2\text{S}/\text{CH}_4$ selectivities determined with the ternary mixture were 94 and 16, respectively. The retentate and permeate compositions determined experimentally agreed well with the values predicted from computer simulations assuming perfect-mixing conditions in the permeability cell. The computer simulations made use of the permeability coefficients obtained from separation measurements at very low stage cuts.

Cellulose acetate (CA) is used as a membrane material for the upgrading of raw natural gas on an industrial scale. All four new polymers evaluated have higher CO_2/CH_4 selectivities than CA.

The D-2 polyimide has a CO_2/CH_4 selectivity that is nearly *2.5 times higher* than that of CA under comparable conditions. The D-2 and G-1 polymers also exhibit higher permeabilities to CO_2 than CA, the permeability coefficient for CO_2 of G-1 being nearly *ten times higher* than that of CA.

Polyimide D-2 and the polypyrrolone G-1 clearly surpass CA in both CO_2/CH_4 selectivity and in CO_2 permeability. The E-1 and F-1 polyimides exhibit higher CO_2/CH_4 selectivity, but their CO_2 permeabilities are 35-45% lower than that obtained with CA. However, higher CO_2/CH_4 selectivities are more important than higher *intrinsic* permeabilities (as characterized by gas permeability coefficients) because high permeation rates can be achieved by decreasing the effective thickness of membranes, that is, by using the membranes in asymmetric or composite forms. Process simulations and economic evaluations that are currently in progress will provide a more quantitative comparison between the performances of the new membranes and CA.

Figure 2. CH_4 , CO_2 , and H_2S in the retentate matched well with predictions.

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