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S. Sircar[a]; M. B. Rao[a]; C. M. A. Thaeron[a]
[a] AIR PRODUCTS AND CHEMICALS, INC., ALLENTOWN, PENNSYLVANIA, USA

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MEMBRANE TECHNOLOGY SYMPOSIUM ARTICLE

Selective Surface Flow Membrane for Gas Separation

S. SIRCAR,* M. B. RAO, and C. M. A. THAERON
AIR PRODUCTS AND CHEMICALS, INC.
7201 HAMILTON BOULEVARD, ALLENTOWN, PENNSYLVANIA 18195-1501, USA

ABSTRACT

The selective surface flow membrane is a nanoporous carbon membrane which separates gas mixtures by a selective adsorption–surface diffusion–desorption mechanism. It selectively permeates the larger and the more polar components of a feed gas mixture. The separation characteristics of several different gas mixtures by the membrane are described. The membrane has been field-tested at a refinery site for separation of hydrocarbon–hydrogen mixtures.

INTRODUCTION

A new class of nanoporous carbon membrane for gas separation called selective surface flow (SSF†) membrane has been developed by Air Products and Chemicals, Inc. (1, 2). It consists of a thin layer (2–3 μm) of a nanoporous carbon matrix (5–7 Å pore diameter) supported on the bore side of a macroporous ($<$1 μm pore diameter) alumina tube (0.56 cm internal diameter, 0.16 cm wall thickness). The membrane is produced by: (a) coating the bore side of the tubular support with a thin uniform layer of a polyvinylidene chloride–acrylate terpolymer latex containing 0.1–0.14 μm polymer beads in an aqueous emulsion (4 wt% solid), (b) drying the coat under N_2 at 50°C, (c) heating under a dry N_2 purge to 600°C for carbonizing the polymer, and (d) passivating the nascent carbon film by heating in an oxidizing atmosphere at 200–300°C. Only a single coat of the latex and a single heating step are used.

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* To whom correspondence should be addressed.
† SSF is a trademark of Air Products and Chemicals, Inc.

A detailed description of the carbonization process is given elsewhere (1–3). The resulting carbon membrane has a very narrow pore-size distribution as characterized by pure CH_4 diffusion (4).

The mechanism of gas transport through the SSF membrane is described by Figure 1. It shows a cartoon of a single idealized carbon pore. The feed gas mixture to be separated is passed over one side of the membrane at a relatively higher pressure (P^{H}), and the other side of the membrane is maintained at a relatively lower pressure (P^{L}). The larger (yet smaller than the carbon pore) and the more polar components of the feed gas mixture are selectively adsorbed on the membrane pore walls at the high pressure side followed by their selective surface diffusion to the low pressure side where they desorb to the low pressure gas phase. Under certain conditions the adsorbed molecules hinder or completely block the flow of nonadsorbed components of the feed gas mixture through the void space between the pore walls. The phenomenon is depicted in Fig. 1 for separation of hydrocarbon (more selectively adsorbed components)–hydrogen mixtures by the SSF membrane.

This unique mechanism of gas transport through the SSF membrane provides the following practical advantages:

(a) The high pressure effluent from the membrane consists of a gas stream enriched in the less selectively adsorbed component of the feed gas mixture which is often the desired product. It is produced at the feed gas pressure. Thus, the need for subsequent compression of this gas for further purification is reduced or eliminated.

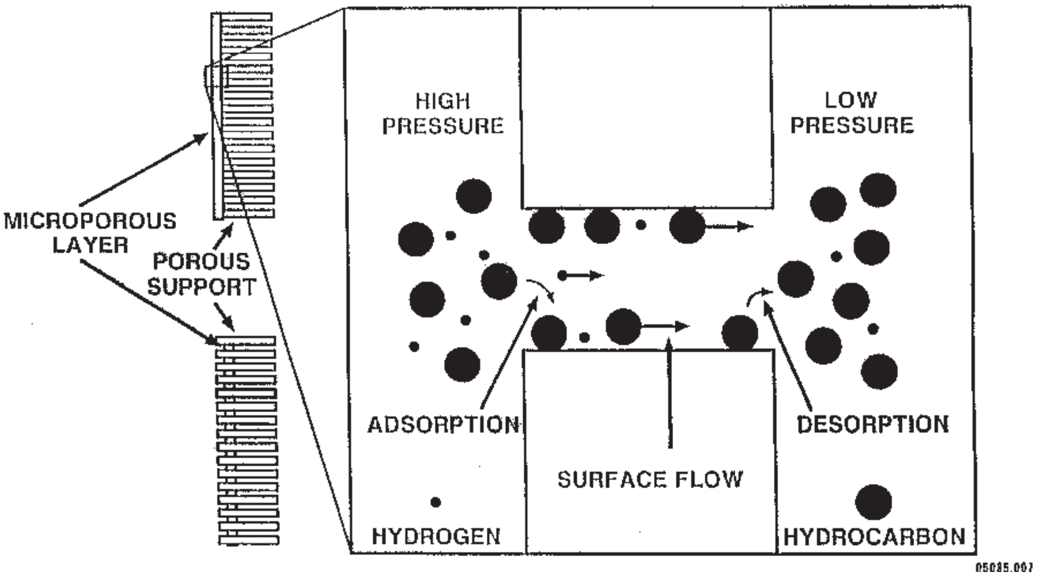

FIG. 1 Concept of gas transport mechanism by SSF membrane. Pore size 5–7 Å; hydrocarbon diameter ~4–5 Å; hydrogen diameter ~3 Å.

(b) The membrane can be operated using a relatively low value of P^H and a near ambient value of P^L because the true driving force for transport of a component of a gas mixture through the pores of the SSF membrane is determined by the specific adsorbate loading gradient across the membrane. A large adsorbate loading of the selectively adsorbed component of the feed gas mixture can be achieved at a relatively low P^H value when it is strongly adsorbed.

(c) The fluxes of the selectively adsorbed components through the SSF membrane can be very high because the energy barriers for surface diffusion of molecules on carbon are relatively low compared to those for transport of gases through a conventional polymeric matrix. The high flux eliminates the need for having ultrathin membranes.

(d) The selectivity of separation between the various components of the feed gas mixture by SSF membrane is governed by (i) the equilibrium adsorption selectively at the high pressure side, (ii) the selective surface diffusion on carbon pore walls, and (iii) the hindered diffusion of the less selectively adsorbed components through the void space between the pore walls.

(e) A combination of properties (c) and (d) can simultaneously provide a high selectivity and a high flux for the transport of preferentially adsorbed components through the SSF membrane.

(f) The adsorptive properties of the SSF membrane can be easily altered by molecular engineering (controlling pore size and surface polarity of the carbon).

EXPERIMENTAL EVALUATION

The performance of the SSF membrane has been experimentally evaluated for several practical gas separation applications. They include: (a) separation of H_2 from gas mixtures containing C_1–C_4 hydrocarbons, (b) separation of H_2 from gas mixtures containing CO_2 and CH_4, (c) separation of binary H_2S–H_2 and H_2S–CH_4 mixtures, and (d) separation of binary CO_2–H_2 mixtures.

A schematic diagram of the experimental set-up used for measuring the performance of the SSF membrane is given by Fig. 2. The membrane tube was mounted inside a membrane holder (2.3 cm internal diameter). The feed gas (pressure P^H) was passed through the bore-side of the membrane tube. The permeate gas (pressure P^L) was countercurrently withdrawn through the shell-side of the holder. The gas flow rates and compositions of high- and low-pressure-side inlet and outlet streams of the membrane system were continuously monitored using mass flow controllers (MFC), bubble flow meters (BFM), and gas chromatographs (GC). The membrane performance data were collected after a steady-state was achieved for each run which typically took half

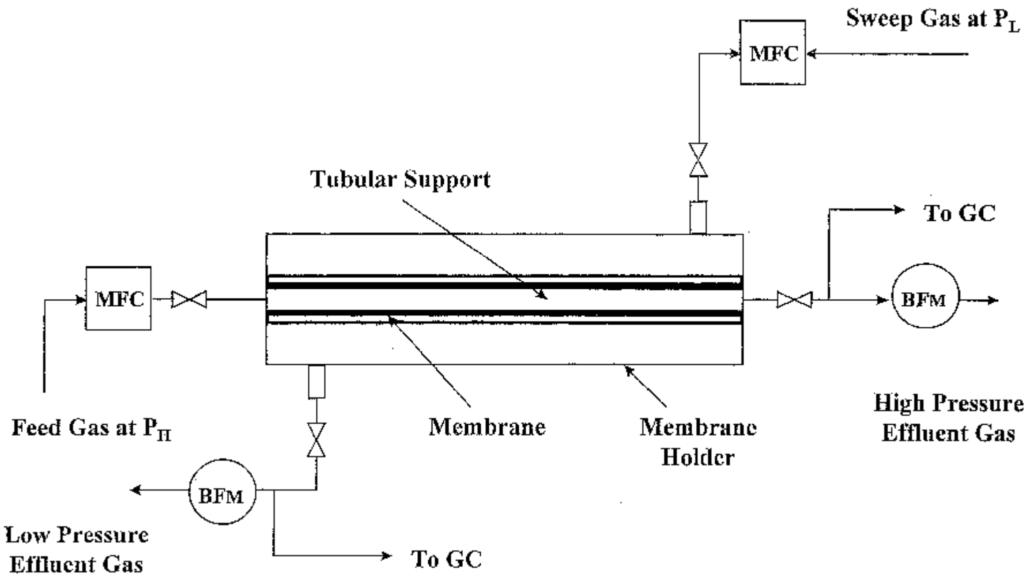

FIG. 2 Schematic diagram of experimental test apparatus: MFC = mass flow controller; BFM = bubble flow meter; GC = gas chromatograph.

an hour of operation. All experiments were conducted at ambient temperature (23 ± 2°C). The overall and component balances checked within ±5%.

DATA REPRESENTATION

The partial pressures of the components of the gas mixture (both high and low pressure sides) vary along the length of the membrane tube under steady-state operation. Thus, the specific adsorbate loadings of the components of the gas mixture and the component adsorption selectivities at the membrane pore mouths, as well as the component surface diffusivities through the membrane pores, vary along the length of the membrane tube. The profiles of these properties along the length of the membrane tube are determined by the values of P^H, P^L, feed gas flow rate and composition, the transport area of the membrane tube, system temperature, etc. Therefore, it is not possible to characterize the separation performance of the SSF membrane in terms of a single permeance or permselectivity property for each component of the gas mixture, which is the common practice for characterizing polymeric membranes.

The SSF membrane is characterized by its actual separation performance. The rejections of the more strongly adsorbed components are described as functions of the recovery of the least strongly adsorbed component. The rejection (β_i) of a more strongly adsorbed component *i* is defined as the fraction

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of that component in the feed gas which leaves the membrane system as the low pressure effluent gas. The recovery (α) of the least strongly adsorbed component is defined as the fraction of that component in the feed gas which leaves the membrane system as the high pressure effluent gas. The flow rates and compositions of all gas streams leaving the membrane can be described by specifying α, β_i, the feed gas flow rate, and its composition (5). Consequently, all separation performance data for SSF membrane reported in this paper will be expressed in terms of the appropriate rejection-recovery (β_i vs α) plots for a given set of P^H and P^L values as well as the feed gas composition. The rejection–recovery plots for each separation system are generated by carrying out different steady-state runs using different feed gas flow rates while maintaining a constant feed gas composition and values of P^H and P^L.

HYDROCARBON–HYDROGEN SEPARATION

Many refinery waste gases contain a low concentration of H_2 (20–40 mol%) along with various concentrations of C_1–C_4 hydrocarbons (saturated and unsaturated). They are available at low to moderate (0.3–1.5 MPa) pressure. Currently, these gases are combusted to recover their heating values because there is no practical and economical means to recover the hydrogen. The SSF membrane can be used to produce an enriched H_2 stream (50–70 mol%) at feed gas pressure from these waste gases by selectively permeating the hydrocarbons through the membrane. The H_2-enriched stream can then be processed in a conventional pressure swing adsorption (PSA) unit to produce a pure H_2 (99.99+ mol%) product stream. Figure 3 represents a schematic flow diagram for such a hybrid process.

For example, a typical fluid catalytic cracker off-gas contains 20% H_2, 20% CH_4, 8% C_2H_4, 8% C_2H_6, 29% C_3H_6, and 15% C_3H_8 at a pressure of 0.3 MPa.

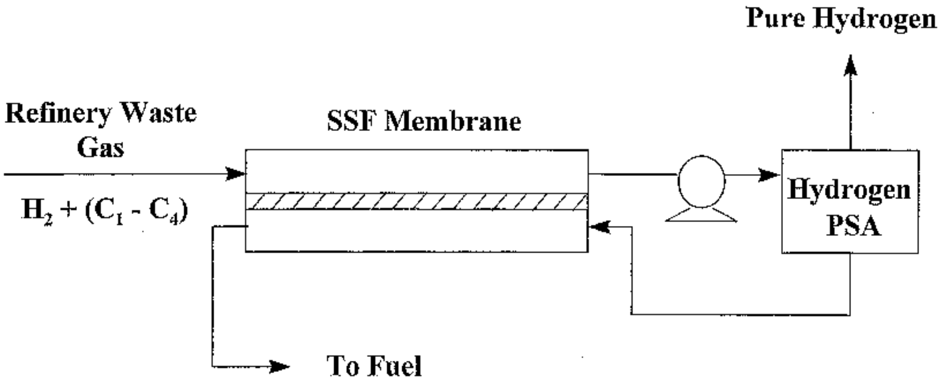

FIG. 3 Schematic diagram of hybrid SSF–PSA process.

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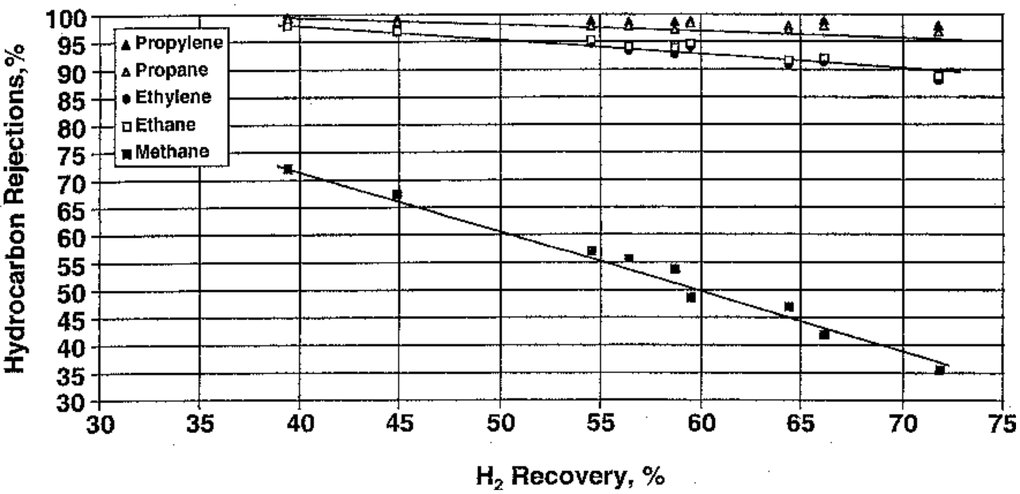

FIG. 4 Separation characteristics of hydrocarbon–hydrogen mixtures.

Figure 4 shows the experimental hydrocarbon rejection–hydrogen recovery plot from such a feed gas by SSF membrane operated using a P^L value of 0.115 MPa (5). A very high rejection of C_2^+ hydrocarbons (C_3H_8 = 98.2%, C_3H_6 = 98.8%, C_2H_6 = 94.1%, C_2H_4 = 93.3%) can be achieved at a H_2 recovery of 60%. The corresponding high pressure effluent gas from the membrane contains 51.6% H_2, 41.5% CH_4, 2.0% C_2H_4, 2.3% C_2H_6, 1.5% C_3H_6, and 1.2% C_3H_8, which can be further compressed and purified in a PSA unit to produce a pure H_2 product. The overall H_2 product recovery from the feed gas by the hybrid process, for this case, is 50%. It is also possible to recover the C_3 hydrocarbons from the SSF permeate stream (C_3 enriched) by their partial condensation.

CARBON DIOXIDE–METHANE–HYDROGEN SEPARATION

The most common route to produce hydrogen consists of steam reformation of natural gas, high and low temperature water-gas shift reactions, and purification of the reaction products (after cooling) using a PSA process. The feed to the PSA process typically contains ~70.5% H_2, 25.7% CO_2, and 3.8% (CH_4 + CO) in a dry basis at a pressure of 1.8 MPa. The pure H_2 product (99.99+ mol%) is produced from the PSA unit at the feed gas pressure with a typical H_2 recovery of ~75–85%. The PSA waste gas is typically produced at a pressure of 0.14 MPa and it contains the balance of feed H_2 as well as all of the feed CO_2, CH_4 and CO impurities. This gas is used as a fuel.

The SSF membrane can be used to substantially increase the effective H_2 recovery from the H_2–PSA feed gas by enriching and recycling a part of the H_2 from the PSA waste gas. The PSA waste gas can be compressed to 0.4 MPa and fed to a SSF membrane system. CO_2 and CH_4 are preferentially permeated through the membrane. The H_2-enriched high pressure effluent gas from the membrane can be further compressed and fed to the H_2–PSA unit by mixing it with the shift-reactor effluent gas. The gas-handling capacity of the PSA system must be increased in order to process the recycled feed stream. Figure 5 shows a schematic flow diagram for the above described concept.

The hybrid process of Fig. 5 operated with a H_2 recovery of 75% in the PSA unit and a H_2 recovery of 60% in the SSF membrane unit would produce a PSA waste gas (feed to SSF unit) containing 35% H_2, 55% CO_2, and 10% (CH_4 + CO). Figure 6 shows the CO_2 and CH_4 rejections as functions of H_2 recoveries at a pressure of 0.4 MPa from such a feed gas to the SSF membrane. The rejection of CO is similar to that of CH_4. The CO_2 and CH_4 rejections are, respectively, 79 and 65% at a H_2 recovery of 60%, and the corresponding high pressure effluent gas contains 58.2% H_2, 32.0% CO_2, and 9.7% (CH_4 + CO). The quantity of the feed gas to the PSA unit is increased by 21.3% due to recycle of H_2-enriched gas from the SSF unit. The net H_2 product from the PSA unit is also increased by 17.6%. This represents an effective H_2 recovery of 88.2% from the shift-reactor effluent gas compared to the original H_2 recovery value of 75%.

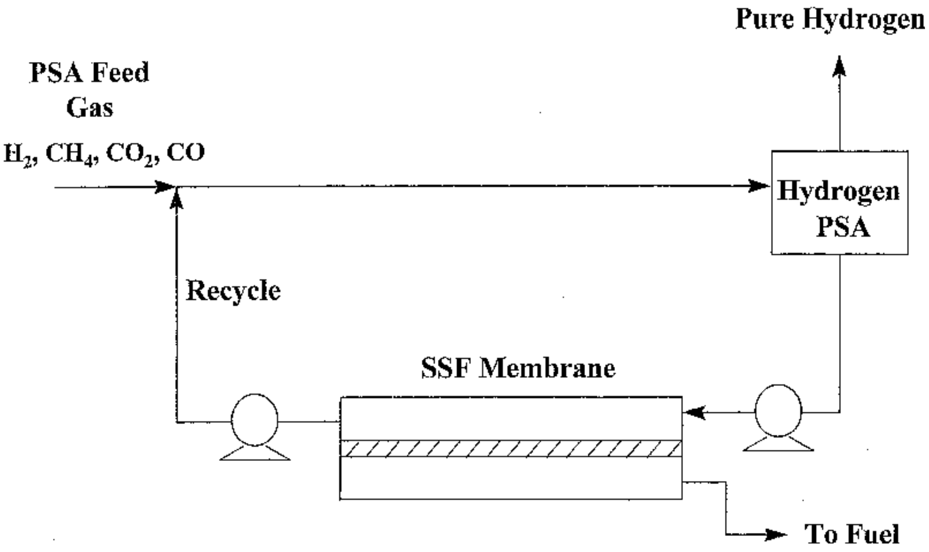

FIG. 5 Schematic diagram of hybrid PSA–SSF process.

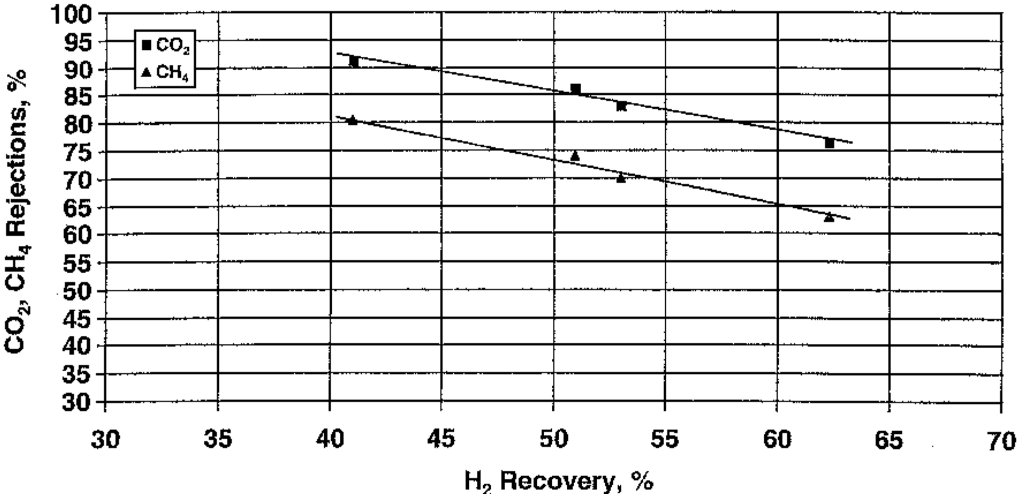

FIG. 6 Separation characteristics of CO_2–CH_4–H_2 mixtures.

HYDROGEN SULFIDE–HYDROGEN (OR METHANE) SEPARATION

Removal of bulk H_2S ($>$20 mol%) from CH_4 or H_2 at a moderate gas pressure ($<$0.8 MPa) can be a major technical hurdle. The SSF membrane offers an opportunity in this area. The membrane selectively permeates H_2S from CH_4 or H_2, providing a high rejection of H_2S at a high recovery of CH_4 or H_2 even when the feed gas pressure is low ($<$0.8 MPa).

Figure 7 shows the H_2S rejection–H_2 recovery characteristics for the SSF membrane using a binary feed gas containing 25 and 50% H_2S at a pressure of 0.79 MPa (6). The H_2S rejection increases for a given H_2 recovery as the partial pressure of H_2S in the feed gas increases. More than 90% rejection of H_2S can be achieved at a H_2 recovery of 70% when the H_2S partial pressure in the feed gas is 0.39 MPa or above.

Figure 8 shows a family of H_2S rejection–CH_4 recovery characteristics for the SSF membrane using a binary feed gas containing 10–50% H_2S at different feed gas pressures (7). A very interesting behavior is that the H_2S rejection–CH_4 recovery plots coincide when the partial pressures of H_2S in the feed gas are the same, irrespective of the total feed gas pressure and its H_2S composition. Again, more than 90% H_2S rejection can be achieved at a CH_4 recovery of 70% when the feed gas H_2S partial pressure is 0.39 MPa or above.

The two-stage SSF membrane described by Fig. 9 can be used to produce a gas stream containing 98+% CH_4 (or H_2) at a low feed gas pressure (0.45 MPa) from an equimolar binary feed gas mixture containing H_2S and CH_4 (or

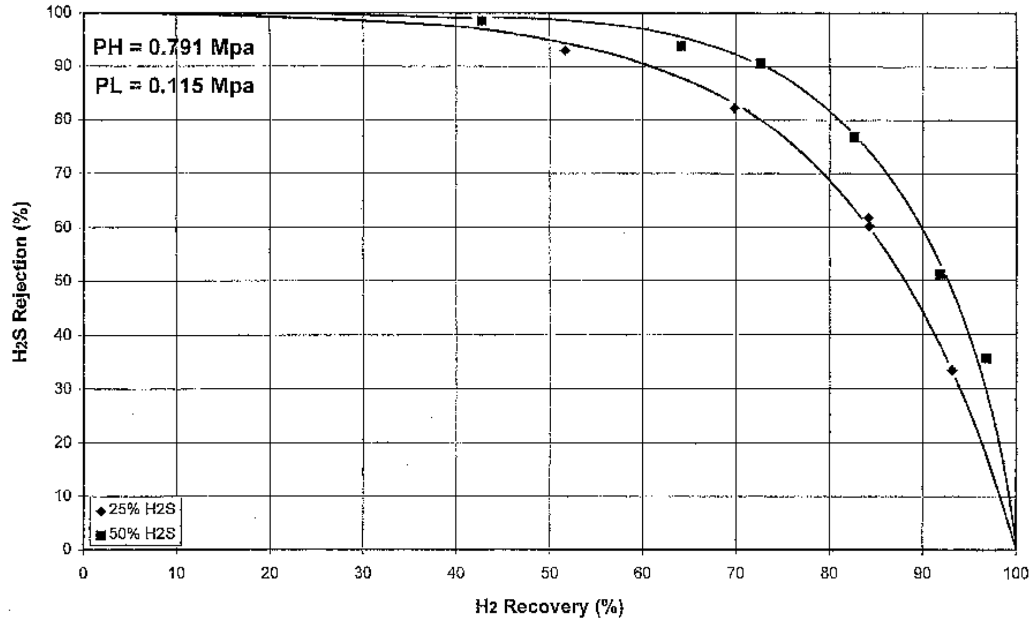

FIG. 7 Separation characteristics of H_2S–H_2 mixtures.

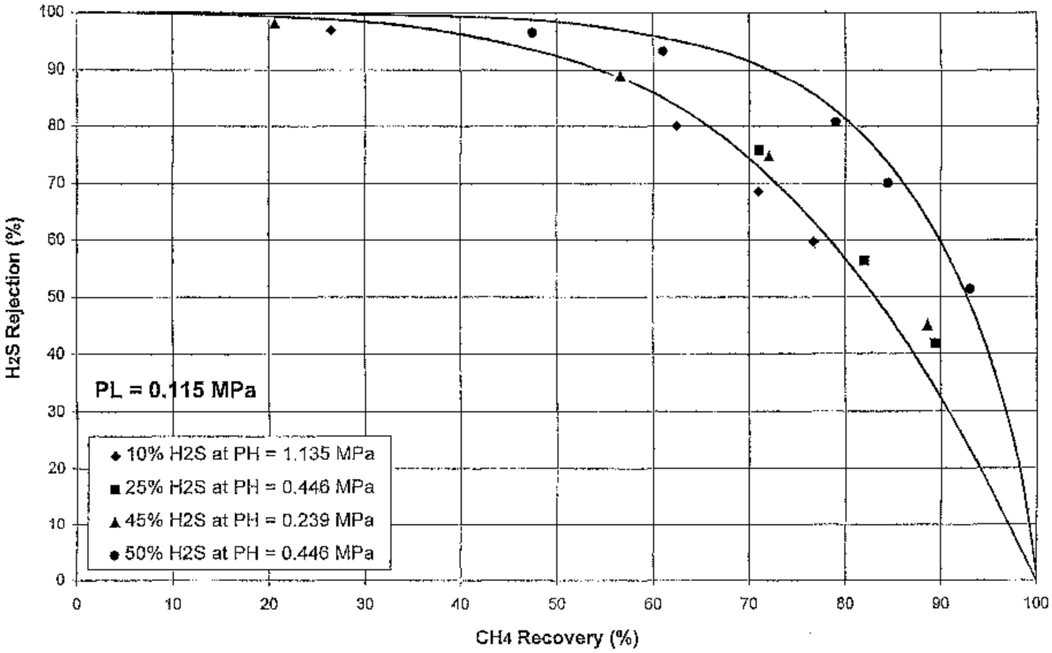

FIG. 8 Separation characteristics of H_2S–CH_4 mixtures.

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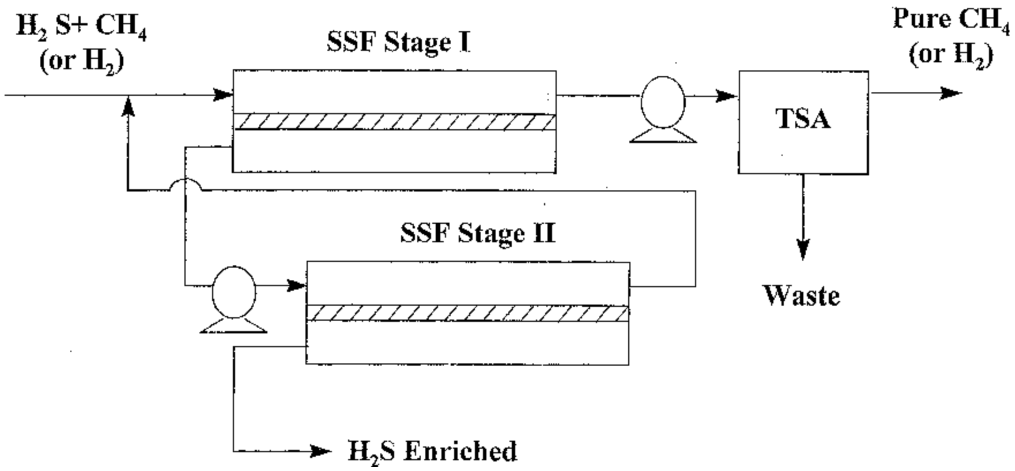

FIG. 9 Schematic diagram of dual stage SSF–TSA hybrid process.

H_2). The low pressure effluent gas from the first stage SSF membrane is compressed and fed to the second stage SSF membrane while the high pressure effluent gas from the second stage SSF membrane is recycled as feed to the first stage membrane. This remarkable separation of H_2S–CH_4 (or H_2) mixture using the SSF membrane can be achieved by using a novel scheme (8) where the first stage is operated with a low H_2 recovery (~30%) while the second stage is operated with a high H_2 recovery (~90%). The 98% CH_4 or H_2 product gas can be further purified to 99.99+ mol% CH_4 or H_2 products using a conventional thermal swing adsorption (TSA) unit. The overall CH_4 or H_2 recoveries (as pure gas) from the equimolar feed gas by the membrane–TSA hybrid processes are, respectively, 73 and 77%, and the overall H_2S rejection by the SSF membrane system alone is 98.3% for both cases.

CARBON DIOXIDE–HYDROGEN SEPARATION

The SSF membrane selectively permeates CO_2 over H_2. Figure 10 is a set of CO_2 rejection–H_2 recovery plots obtained by using binary feed gas mixtures of different compositions at a constant pressure of 1.13 MPa (9). Again, the CO_2 rejection for a given H_2 recovery increases as the CO_2 partial pressure in the feed gas increases. More than 80% rejection of CO_2 can be achieved at a H_2 recovery of 70% when the feed gas CO_2 partial pressure is 0.56 MPa or above. The CO_2 rejection–H_2 recovery plots for different feed gas partial pressures of CO_2 also coincide when the CO_2 partial pressures of the feed gases are the same, irrespective of total gas pressure and its composition (9).

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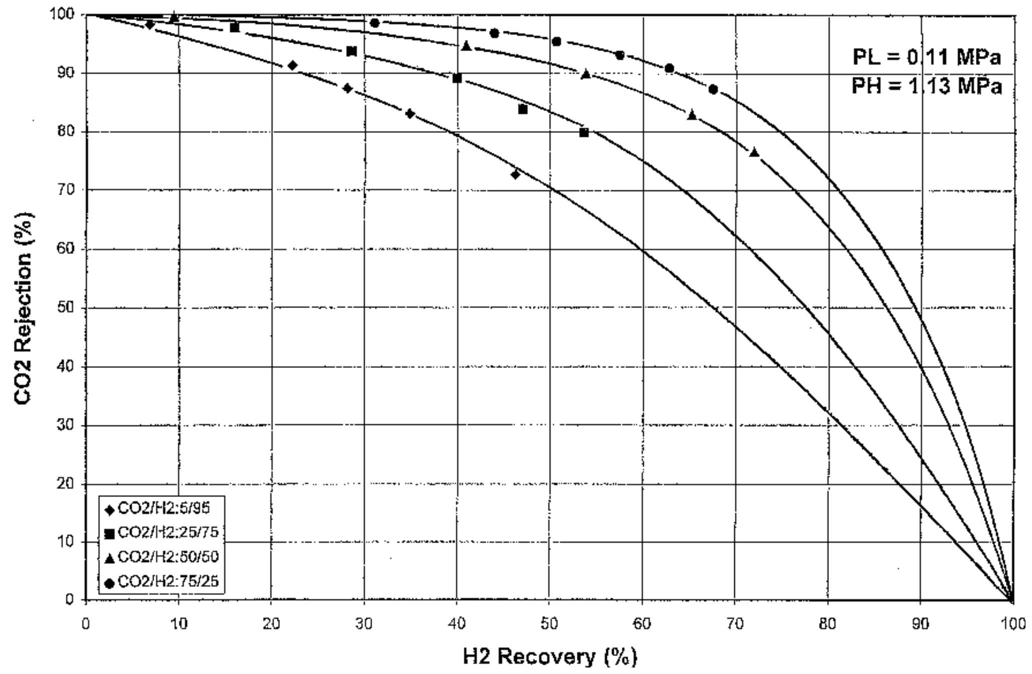

FIG. 10 Separation characteristics of CO_2–H_2 mixtures.

SCALE-UP OF SSF MEMBRANE

A bundle of SSF membrane tubes (each 106 cm long) in a modular form was field-tested at a refinery site for separation of hydrogen–hydrocarbon mixtures (10). The feed gas to the membrane module was supplied at a constant pressure (0.5 MPa) but its composition (14–30% H_2, 35–50% CH_4, 7–15% C_2H_6, 5–7% C_2H_4, 2–7% C_3H_8, and 2–7% C_3H_6) and temperature (10–30°C) fluctuated randomly during the field test. The measured hydrocarbon rejections as functions of H_2 recovery from the field unit fluctuated in a consistent fashion as the feed gas composition changed periodically, but no degradation of the membrane performance was observed during 9 months of continuous operation. The performance of the modular SSF membrane in the field was actually better than that exhibited by a single tube operated under laboratory conditions. This may be caused by better quality control in the production of SSF membrane tubes during mass production. Figure 11 shows an example of the comparative performance (C_3H_8 rejection vs H_2 recovery) between the field test unit and a laboratory scale unit.

The SSF membrane is now undergoing another level of scale-up in the modular form. Figure 12 shows a photograph of a semicommercial SSF membrane unit under construction at a refinery site.

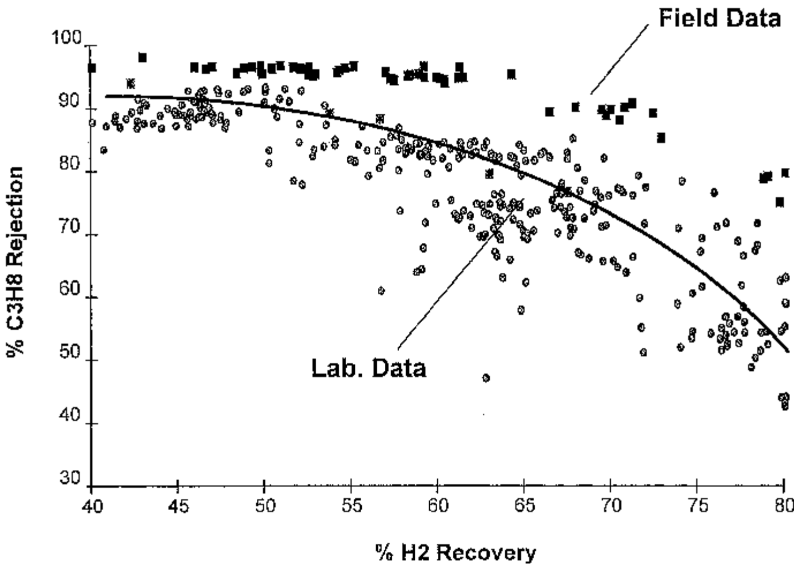

FIG. 11 Comparative performance of field and bench-scale units.

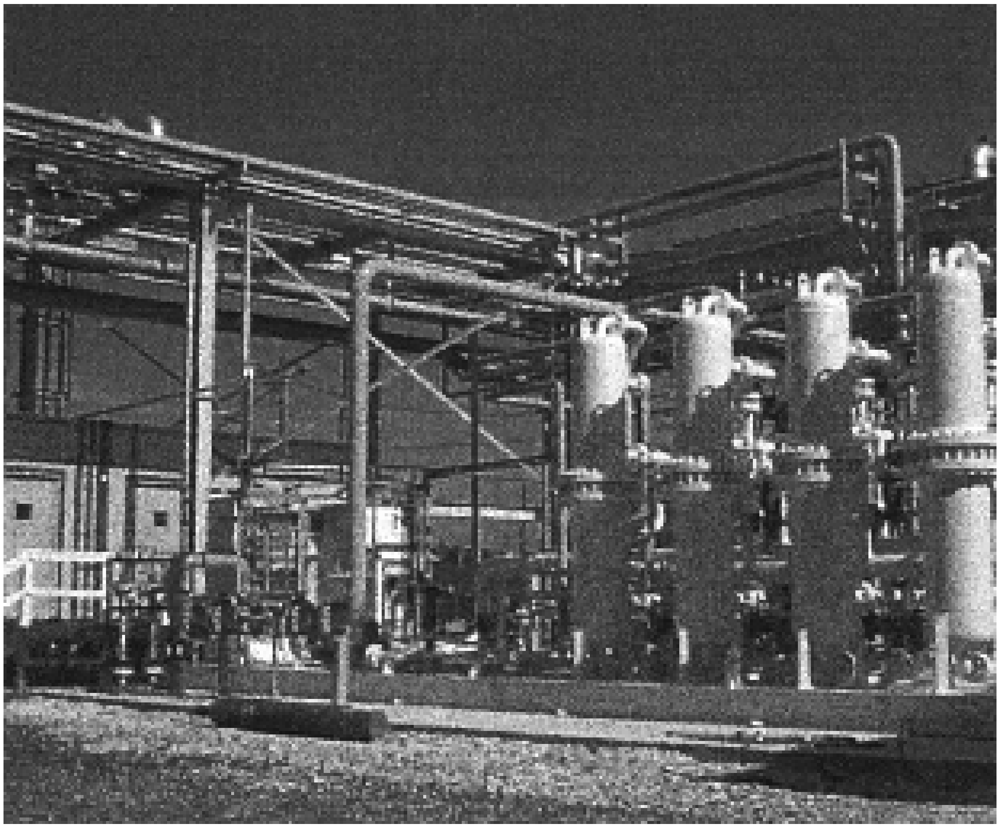

FIG. 12 Semicommercial SSF unit.

CONCLUSIONS

The selective surface flow (SSF) membrane can be used in a variety of industrial gas separations. The selective adsorption–surface diffusion–desorption mechanism of transport through the nanoporous carbon membrane permits the recovery of the less strongly adsorbed components of a feed gas mixture in the high pressure effluent stream while producing a more strongly adsorbed component rich gas as the permeate stream. The membrane exhibits very high separation selectivity at low to moderate feed gas pressures. It has been successfully pilot tested at a refinery site.

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