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Scale-Up of Selective Surface Flow Membrane for Gas Separation

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ABSTRACT

The Selective Surface Flow (SSF) membrane, consisting of a nanoporous carbon layer supported on a macroporous alumina tube, can be used to enrich hydrogen from a feed gas containing hydrogen and hydrocarbon mixtures. The membrane produces a hydrogen-enriched product stream at feed gas pressure by selectively rejecting the hydrocarbons to the low pressure side of the membrane. Bench-scale testing of the membrane showed that very high rejections of C_2^+ hydrocarbons can be achieved from a feed gas containing low concentrations of hydrogen at moderate pressure. The membrane has been scaled-up in length and field-tested in modular form using a real refinery waste gas under actual operating conditions. It successfully tracked the performance of the bench-scale unit under field conditions. Both bench-scale and field-scale performance data are described. Six months of continuous operation in the field did not exhibit any degradation of membrane performance.

INTRODUCTION

The Selective Surface Flow (SSF) membrane is a nanoporous carbon membrane for separation of gas mixtures which is being developed by Air Products and Chemicals, Inc. (1–3). It consists of a thin (2–3 μm average) layer of a nanoporous carbon (5–7 Å effective pore diameter) supported on a macroporous alumina tube (0.2–1.0 μm effective pore diameter). The membrane is produced by coating the support tube with a single layer of

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a polyvinylidene chloride (PVDC) latex film and subsequently carbonizing the polymer (1–3). The uncarbonized PVDC coating is typically 10 μm in thickness and the carbonized film strongly adheres to the support tube without any defect (cracks or flaking).

The transport of gases across the carbon membrane is governed by an adsorption–surface diffusion–desorption mechanism as depicted by Fig. 1 (1). The figure shows the cartoon of a single idealized nanopore across the carbon membrane. A multicomponent gas mixture (feed) is passed at a relatively higher pressure (P^H) over one side of the carbon membrane and the other side of the membrane is held at a relatively lower pressure ($P^L < P^H$). The more polar and the larger molecules (smaller than the membrane pore size) of the feed gas mixture are selectively adsorbed on the membrane pore walls. The adsorbed molecules selectively diffuse on the pore wall surface to the low pressure side of the membrane, where they desorb into the gas phase at pressure P^L (1). Consequently, the membrane produces a gas mixture enriched in the less polar and the relatively smaller molecules of the feed gas mixture as the high pressure effluent at pressure P^H, and a gas mixture enriched in the more polar and the relatively larger

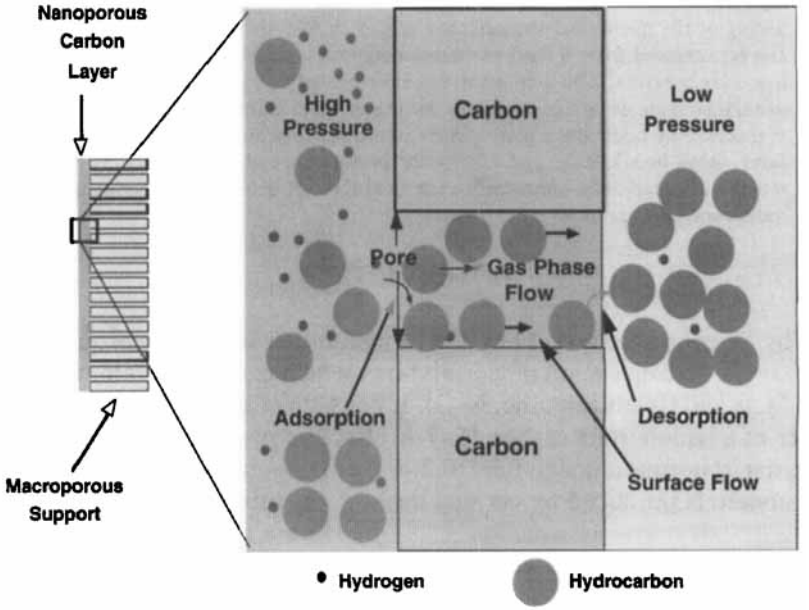


FIG. 1 Schematic diagram of SSF membrane gas transport mechanism.

molecules of the feed gas mixture as the low pressure effluent at pressure P^L. This is in contrast with the gas permeation characteristics of most polymeric membranes where the relatively smaller molecules of a gas mixture are selectively permeated from the high to the low pressure side. The separation of a hydrogen (less selectively adsorbed)–hydrocarbon (more selectively absorbed) mixture is described as an example by Fig. 1. It will be shown later that the SSF membrane exhibits excellent separation performance for this mixture.

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

(a) It can be operated using a relatively small pressure gradient across the membrane because the true driving force for transport of a component of a gas mixture is determined by the specific adsorbate loading difference inside the membrane nanopores between the high and low pressure sides. A large adsorbate loading of the selectively adsorbed component can be obtained at the high pressure side at a relatively low absolute pressure (P^H) when that component is strongly adsorbed.

(b) The fluxes of the adsorbed components through the membrane can be high relative to polymer membranes because the energy barriers for surface diffusion are relatively low compared to the energy barriers for the transport of gases through a polymeric matrix.

(c) The adsorbed molecules can significantly hinder or completely block the flow of nonadsorbed components through the void space within the carbon pores when the pore sizes are comparable to the sizes of the adsorbed molecules.

(d) A combination of selective adsorption at low pressure (a) and selective but fast transport of adsorbed molecules (b and c) through the SSF membrane pore provides the desired property of high separation selectivity and high permeability of the adsorbed molecules.

(e) The high permeability of the adsorbed molecules precludes the requirement of a very thin membrane for high permeance through the membrane. A membrane thickness of 1–5 μm is acceptable.

(f) The high pressure effluent from the membrane consists of a gas stream which is enriched in the less selectively adsorbed component of the feed gas mixture (e.g., H_2 from a hydrocarbon mixture). This can be a major advantage when the less selectively adsorbed component of the feed gas is the desired product, because it will reduce or eliminate subsequent compression for further purification and use of the product.

(g) The adsorptive characteristics of the carbon nanopores can be easily altered by molecular engineering (controlling pore size and pore surface polarity).

LABORATORY-SCALE PERFORMANCE OF SSF MEMBRANE

The SSF membranes were prepared for laboratory-scale testing by using macroporous alumina tubes as supports. The tubes were 30 cm long, and the inside and outside diameters were 6 and 9 mm, respectively. The details of preparation methods are given elsewhere (1–3). It was found that the membrane performed extremely well for enriching hydrogen from a multicomponent gas stream containing (a) 20% H_2, 20% CH_4, 8% C_2H_4, 8% C_2H_6, 29% C_3H_6, and 15% C_3H_8 and (b) 35% H_2, 55% CO_2, and 10% CH_4 (4). Gas streams (a) and (b) are typical representations of waste gases from refinery operations and from Pressure Swing Adsorption (PSA) processes for hydrogen production from steam–methane–reformer effluent, respectively. Both gases contain low quantities (20–40 mol%) of H_2 (less selectively adsorbed) and bulk quantities (60–80 mol%) of heavier hydrocarbons and carbon dioxide (more strongly adsorbed). Both gases are typically available at low to moderate pressure (1–5 atm).

Figure 2 shows the separation performance of the SSF membrane from feed gas (a) described above at a pressure of 3.0 atm and at a temperature of 295 K (4). The figure shows rejections of C_1–C_3 hydrocarbons (saturated and unsaturated) as functions of H_2 recovery using a laboratory-scale membrane. The hydrocarbon rejection is defined by the fraction of feed hydrocarbon leaving the membrane in the low pressure side effluent.

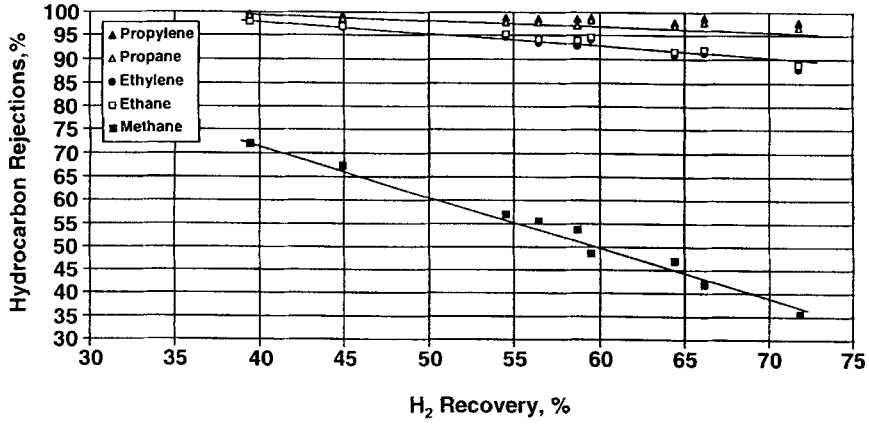


FIG. 2 Performance of bench-scale SSF membrane unit for hydrogen–hydrocarbon separation.

The hydrogen recovery is defined by the fraction of feed hydrogen leaving the membrane in the high pressure side effluent. The data of Fig. 2 were measured using a countercurrent flow pattern between the high and low pressure sides of the tubular membrane and using a pure methane sweep at the entrance end of the low pressure side. The high pressure feed gas was introduced into the bore side of the tubular membrane, and the low pressure permeate was collected at the shell side of the membrane module. The permeate side pressure was maintained at 1.0 atm and the ratio of sweep to feed gas molar flow rates was 0.15. The hydrogen recovery and the corresponding hydrocarbon rejections were varied by changing the feed gas flow rate into the membrane while keeping the feed gas composition and pressure constant. The system temperature was ambient. The feed gas mass flow rates through the membrane tubes were varied from 0.13 to 0.67 mg mol/cm^2/s in order to change H_2 recovery from 40 to 70%. The bench scale data mass balances (overall and component) checked within $\pm 3.0\%$.

It may be seen from Fig. 2 that the rejections of hydrocarbons from the feed gas increased in the order $C_3H_8/C_3H_6 > C_2H_6/C_2H_4 > CH_4$, which is also the order of relative strengths of adsorption of the hydrocarbons on the carbon membrane. In particular, the rejections of C_2 and C_3 hydrocarbons by the membrane for a given H_2 recovery were very high. The rejection of CH_4 was relatively low. There were not much differences between the rejections of saturated and unsaturated hydrocarbons (both C_2 and C_3). The hydrocarbon rejection increased as the H_2 recovery was decreased. However, a very decent rejection of higher hydrocarbons (>90%) could be obtained even at a fairly high H_2 recovery (60–70%).

Table 1 reports the hydrocarbon rejections at a hydrogen recovery of 60% according to Fig. 2. It shows that hydrocarbon rejections of (a) more than 98% for propane and propylene, (b) 94% for ethane and ethylene, and (c) 51% for methane can be achieved from a typical refinery waste feed gas at very low pressure. The rejection–recovery data of Fig. 2 can be used to calculate the mole fraction of component i (y_i^H) in the high pressure effluent gas from the membrane (4):

$$y_i^H = y_i^F(1 - R_i)/[\sum y_i^F(1 - R_i)] \quad (1)$$

where y_i^F is the mole fraction of component i in the feed gas and R_i is the rejection of that component by the membrane. The recovery of H_2 is simply given by $(1 - R_{H_2})$. The summation in Eq. (1) is over all components. Thus, according to Table 1, the composition of the high pressure effluent gas (at about 3.0 atm) from the membrane at a 60% H_2 recovery is about 51.3% H_2, 41.9% CH_4, 2.0% C_2H_4, 2.0% C_2H_6, 1.8% C_3H_6, and

TABLE 1
Hydrocarbon Rejections from a Simulated Refinery Waste Gas Feed by Laboratory SSF Membrane Tube at a H_2 Recovery of 60%

Hydrocarbons	Feed gas composition (mol%)	Rejections (%)
C_3H_8	15.0	98.2
C_3H_6	29.0	98.8
C_2H_6	8.0	94.1
C_2H_4	8.0	93.3
CH_4	20.0	52.0
H_2	20.0	40.0

1.0% C_3H_8. Consequently, there is a 2.5-fold enrichment of H_2 composition and more than a 15-fold decrease in the C_3 hydrocarbon compositions in the H_2-enriched effluent from the membrane while obtaining a 60% H_2 recovery by the membrane from a low pressure feed gas.

The high pressure membrane effluent gas can be further purified in a conventional PSA process in order to produce a 99.99+ mol% pure H_2 stream (1, 2). It may be necessary to compress the feed gas to the PSA unit to a pressure level of 8–20 atm in order to achieve high separation efficiency [small adsorbent inventory and high (>80%) H_2 recovery]. It should be noted here that the absence of large quantities (<2 mol%) of C_2 and C_3 hydrocarbons in the high pressure membrane effluent, which is the subsequent feed gas to the PSA unit, significantly reduces the separation duty of that process. Higher hydrocarbons are strongly adsorbed and consequently they are difficult to desorb in the PSA operation (5). Separation of bulk H_2 and CH_4, which consists of more than 92% of the gas mixture as the feed to the PSA unit in the present case, is relatively easier to separate by PSA.

The SSF membrane–PSA hybrid scheme described above is very attractive for recovery and production of H_2 at high purity from a waste gas containing a low concentration of H_2 at low pressures. The direct use of a PSA system for recovering H_2 from such a stream is not viable (5) because of (a) low net H_2 recovery, (b) difficulty to desorb large quantities of heavier hydrocarbons, and (c) high energy needed to compress the bulk impurities to the PSA feed gas pressure. Conventional polymeric membranes are not attractive because of (a) selective permeation of H_2 from the hydrocarbons to the low pressure side requiring substantial recompression for further purification of H_2, and (b) feed gas compression

to 10–30 atm for efficient operation of the membranes. Unconventional polymeric membranes like PTMSP (polytrimethylsilylpropyne) selectively permeate the hydrocarbon over H_2 (4), but their hydrocarbon rejection–hydrogen recovery characteristics for the above described separations are not as favorable as those of the SSF membrane (4). PTMSP may also not be stable under process conditions (6).

SCALE-UP OF SELECTIVE SURFACE FLOW MEMBRANE

It was decided to scale-up the SSF membrane for field testing using a real refinery waste gas under actual operating conditions. A number of tubular membranes were produced using identical alumina supports and preparation methods as those for production of laboratory-scale tubes. The only differences for the field test unit were that (a) the tubes were 106 cm long, (b) a bundle of tubes was used in a modular form, and (c) no sweep gas was used at the low pressure side. The SSF membrane module was installed at a refinery site (TOSCO refinery in California). A refinery waste gas containing 14–30% H_2 and C_1–C_3 hydrocarbon impurities (both saturated and unsaturated C_2 and C_3 hydrocarbons) at a pressure of 5.0 atm was used as the feed gas. The feed was passed through a conventional two column Thermal Swing Adsorption (TSA) unit for removal of heavier hydrocarbons (C_5^+, ring compounds, etc.) and water prior to its introduction to the bore side of the SSF membrane module. The heavier hydrocarbons were removed by a layer of a commercial activated carbon adsorbent, and the water was removed by a layer of commercial activated alumina in the TSA columns. Regeneration of the TSA adsorbents was carried out by heating them to 175°C under clean N_2 flow. The TSA system provided a C_5^+-free feed gas at a dewpoint of -40°C. The feed gas mass flow rates through the membrane tubes were varied from 0.57 to 0.95 mg mol/cm^2/s. The product flow rates can be easily calculated by mass balance using the rejection–recovery data. Figure 3 shows a picture of the membrane module-TSA assembly.

The module was continuously operated for more than 6 months without any degradation in the separation performance Figures 4a–c show the variation in feed gas composition and temperature to the SSF membrane module over an arbitrarily chosen period of 230 hours of operation. The H_2 and CH_4 mole fractions of the feed gas varied between 14 to 30% and 35 to 50%, respectively, during that period. The variations in the compositions of ethane (7–15%), ethylene (5–7%), propane (2–7%) and propylene (2–7%) were relatively small during that period. The feed gas temperature varied between 283 to 303°K.

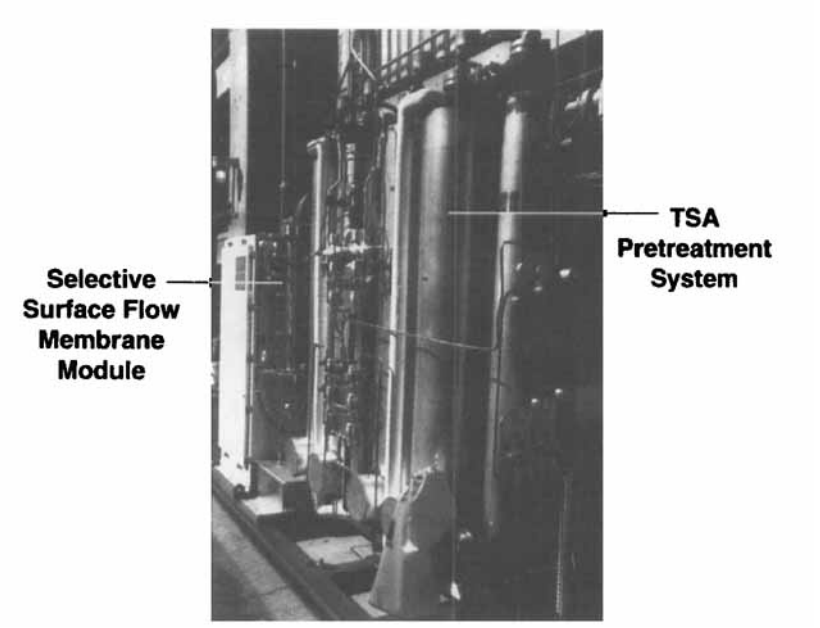


FIG. 3 Picture of the field SSF membrane test unit.

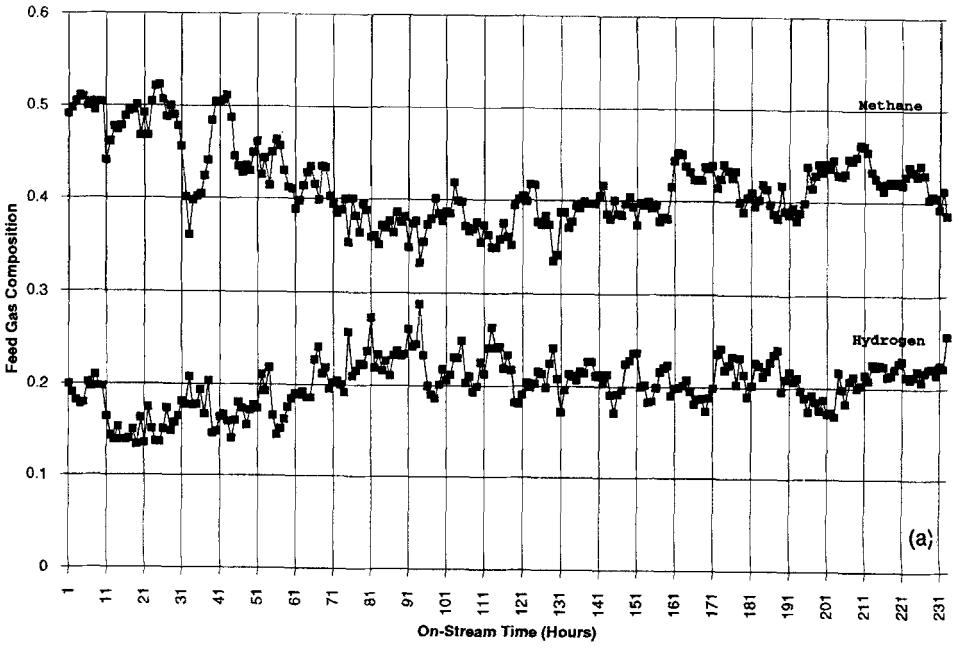
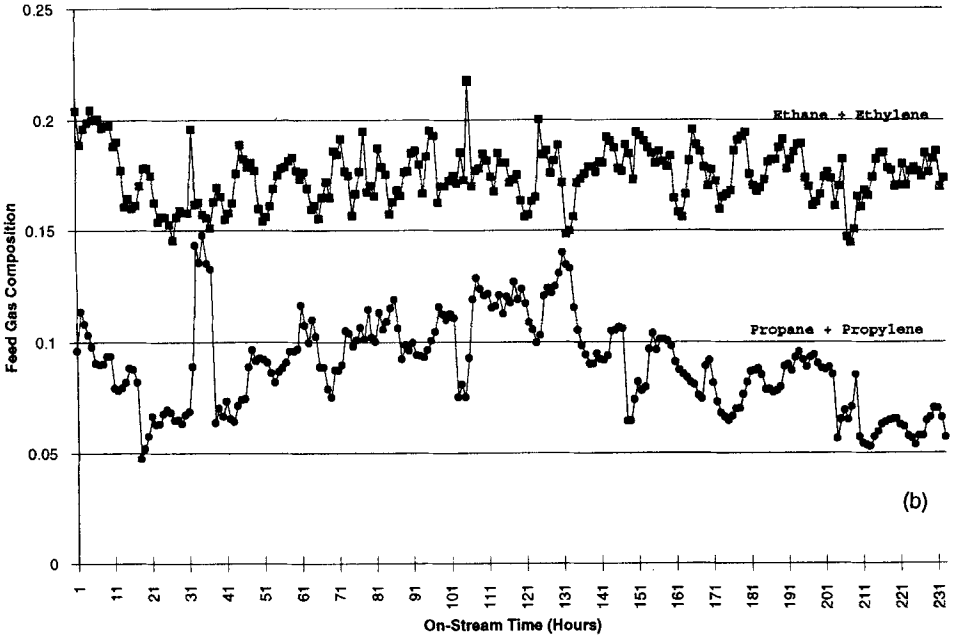


FIG. 4 Variation in feed gas composition and temperature with time to the SSF field unit: (a) Hydrogen and methane composition. (b) Ethane + ethylene and Propane − propylene composition, (c) Temperature.



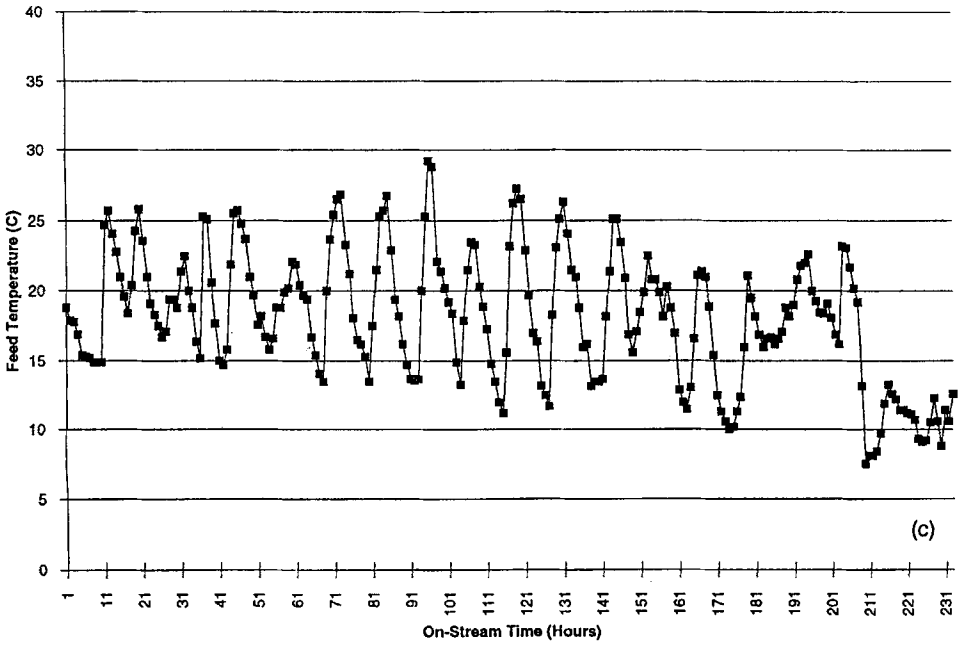


FIG. 4 Continued

Figures 5–9 show the C_3H_8, C_3H_6, C_2H_6, C_2H_4, and CH_4 rejections as functions of H_2 recovery in the field test unit, respectively. The data band in the figures is caused by fluctuations in feed gas composition and temperature. The performance of the membrane changed in a consistent fashion as the feed gas composition changed periodically.

Table 2 reports the range of hydrocarbon rejections achieved by the field SSF membrane module (Figs. 5–9) at an average H_2 recovery value of 60%. The variation in the hydrocarbon rejection values is caused by the variation in the feed gas flow rate, composition, and temperature, as well as by errors in the measurement of these variables. The separation performance of the membrane described by Figs. 5–9 did not change over 6 months of continuous operation.

It may be seen from Table 2 that the field SSF test module very well tracked the performance of the laboratory-scale SSF tube performance (Table 1), even though the feed gas compositions, pressures, and temperatures, as well as the fluctuations of these variables between the two test conditions, were very different.

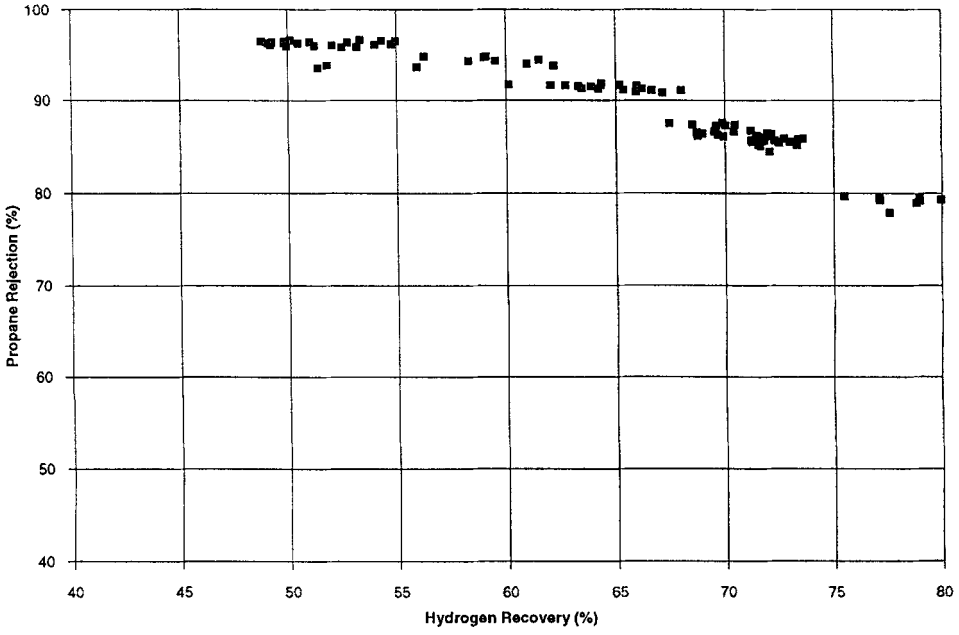


FIG. 5 Rejection of propane as a function of hydrogen recovery by the field test unit.

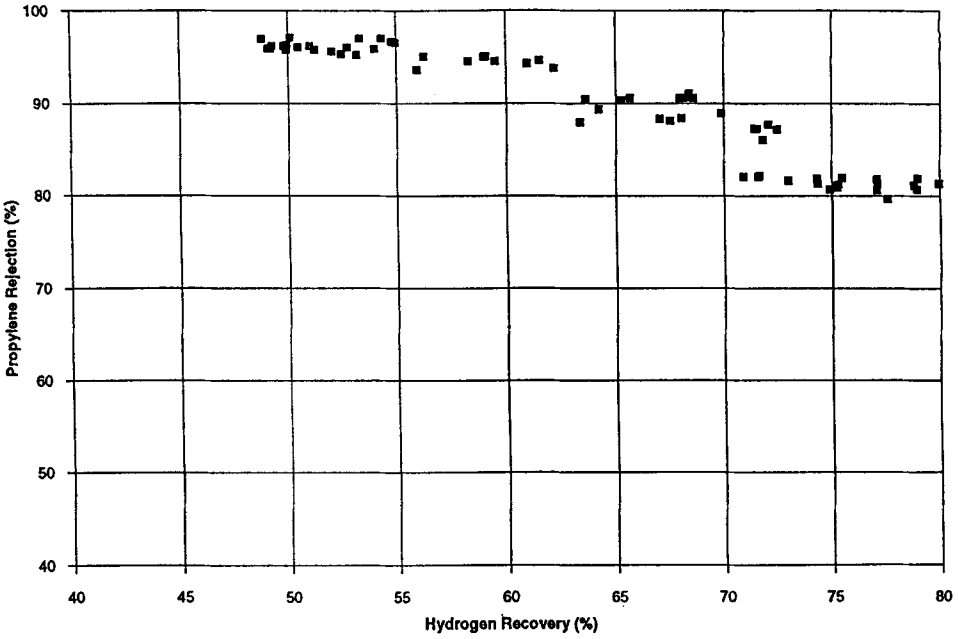


FIG. 6 Rejection of propylene as a function of hydrogen recovery by the field test unit.

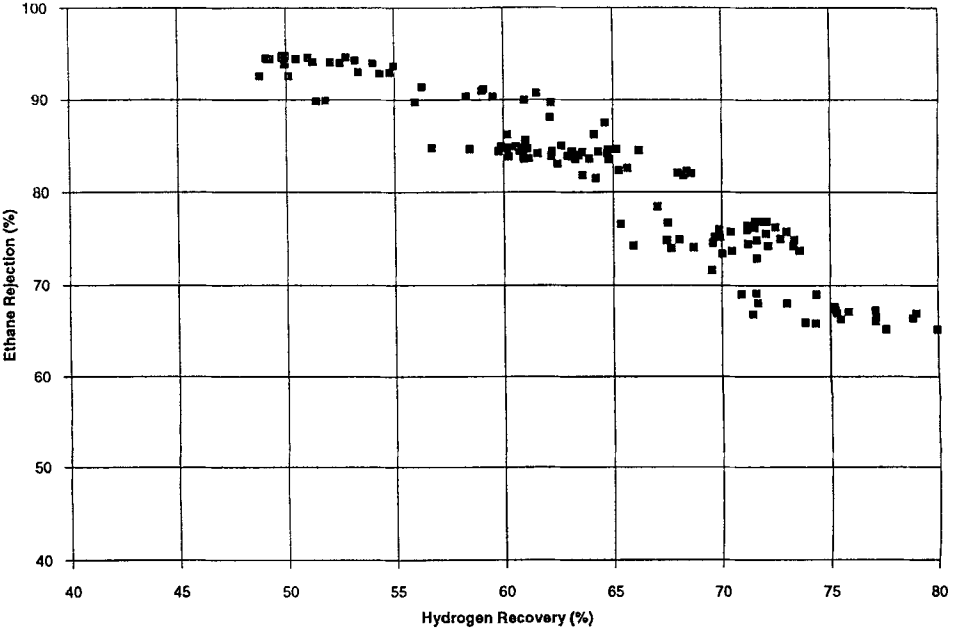


FIG. 7 Rejection of ethane as a function of hydrogen recovery by the field test unit.

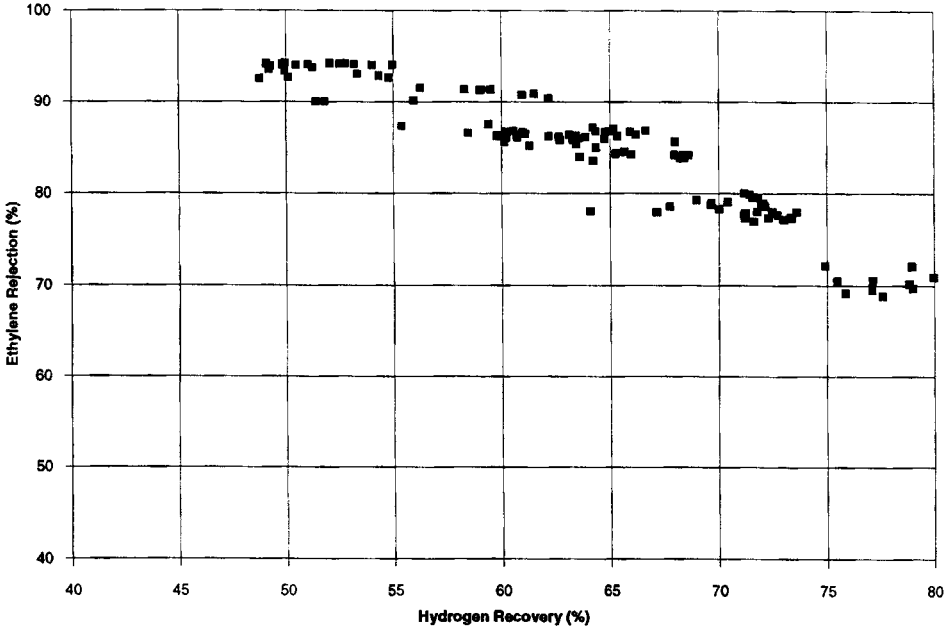


FIG. 8 Rejection of ethylene as a function of hydrogen recovery by the field test unit.

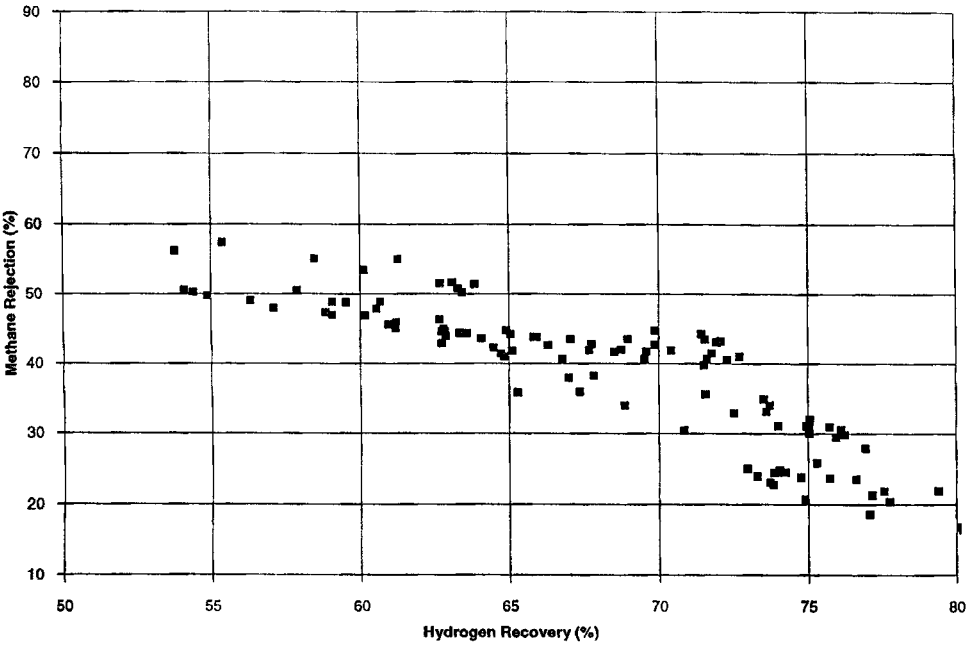


FIG. 9 Rejection of methane as a function of hydrogen recovery by the field test unit.

TABLE 2
Hydrocarbon Rejections from the Field Refinery Waste Gas Feed by the SSF Membrane Module at a Hydrogen Recovery of 60%

Hydrocarbons	Feed gas composition (mol%)	Rejections (%)
C_3H_8	2–7	94
C_3H_6	2–7	94.5
C_2H_6	7–15	84–91
C_2H_4	5–7	86–91
CH_4	35–50	47–55
H_2	14–30	40

CONCLUSIONS

The Selective Surface Flow (SSF) membrane has been successfully scaled-up in a modular form and field tested using a real refinery waste gas containing a hydrogen–hydrocarbon mixture. The membrane can be used to enrich hydrogen by selectively rejecting the hydrocarbons (saturated and unsaturated). Very high rejections (90+%) of higher hydrocarbons (C_2^+) at a high hydrogen recovery (60+%) can be achieved from a feed gas containing low concentrations of H_2 (20–50 mol%) at a moderate feed gas pressure (3–5 atmospheres). The enriched H_2 stream is produced at the feed gas pressure. The membrane can be used in conjunction with a PSA process in order to produce high purity H_2 product from a refinery waste gas. The field performance of the scaled-up SSF membrane tracked the bench-scale performance very well and showed no evidence of degradation over the 6-month test period.

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