1.0 EXECUTIVE SUMMARY

Selective Surface Flow (SSF^{TM}) is a novel carbon membrane developed by Air Products and Chemicals Inc. This membrane separates by selective adsorption and surface diffusion through the membrane porosity. This mechanism imparts separation and selectivity properties not achievable in conventional membranes. Thus, from a mixture of hydrogen and hydrocarbons, the hydrocarbons are selectively permeated through the membrane and the hydrogen is enriched on the non-permeate side and can subsequently be purified to a high purity H_2 stream using a H_2 pressure swing adsorption (PSA) system. The membrane concept was demonstrated on a sheet membrane prior to initiation of this program.

In the first phase of the work, the focus of which was exploratory development of scale-up technology, the architecture of the membrane to be scaled up was defined. It consists of alumina tubes that are internally coated with a thin layer of the carbon membrane. The tubes are assembled in a shell-and-tube housing, and the module is used in a vertical configuration. The gas to be separated is fed into the tube bore from the bottom of the module, and the hydrogen-rich product is collected at feed pressure from the top end of the module. The permeate is collected on the shell side using a counter-current sweep.

The following were the specific achievements in Phase I of the program :
(i) A low cost alumina support was developed for the membrane coating.
(ii) A reproducible coating process was developed for SSF membrane preparation.
(iii) Tubular membrane separation and permeability properties exceeded the benchmark from sheet membranes, and the levels set as the target in the proposed work.
(iv) A large number of tubes were prepared for a multi-tube module containing 19 tubes and representing a 1 ft^2 membrane area.
(v) A multi-tube module (19 tubes) with 1 ft^2 membrane area was designed and built.
(vi) A system for evaluating the performance of the multi-tube module was designed and built.
(vii) Mixed gas performance data were generated in the laboratory on the multi-tube module and used for process design.
(viii) Effects of flow direction on membrane performance were investigated and the preferred conditions for membrane operation defined.
(ix) Effects of feed flow rate and temperature on membrane performance were studied and temperature coefficients for H_2 recovery and propylene rejections were calculated.
(x) First pass process design for recovery of H_2 from FCC waste gas was completed.
(xi) First pass economic analysis indicated that recovery of hydrogen from an FCC waste stream represents a 50% reduction in capital cost and a 15% reduction in energy cost.
(xii) Energy savings and waste reduction were calculated for the year 2010, and significant energy savings and reductions in CO_2 and NO_X emissons are projected.

In Phase I all targets were exceeded and the work was completed on time and within cost.

2.0 SELECTIVE SURFACE FLOW (SSF) MEMBRANES

2.1 Objectives

The objective of Phase I was to address various exploratory development issues in the scale-up of the SSF membrane. This included developing (i) an appropriate support for membrane coating, (ii) coating methods and equipment for membrane preparation, (iii) a consistent membrane preparation technique, (iv) membrane performance characteristics, (v) a housing for multi-tube assembly, (vi) membrane test equipment and (vii) process design and first pass economics for hydrogen recovery from waste streams. The project plan and the milestones are shown in Appendix I.

2.2 SSF Background Technology

SSF membranes are a novel class of gas separation membranes developed by Air Products and Chemicals Inc. that represent a paradigm shift in gas separations. These membranes are capable of simultaneously achieving combinations of high separation selectivity and permeability (1,2). These separation characteristics are due to the selective adsorption and surface flow mechanism by which separation of gases occurs in this membrane (1,2). Conventional membranes separate gases by mechanisms such as solution diffusion, size sieving, Knudsen diffusion, and capillary condensation where combinations of high selectivity and permeability are not achieved. In practical conventional membranes with the desired selectivity, the permeabilities are low such that membranes with sub-micron wall thickness are necessary to achieve the desired flux to make the membrane economical. This requires the use of membrane repair techniques so that membrane performance can be maintained. In addition, conventional membranes are operated at relatively high feed pressures (i.e., 150-500 psig) to maintain a high flux through the membrane, especially when the permeating species are present in low concentrations in the feed.

For SSF membranes, separation occurs by selective adsorption of the permeating species at the membrane pore mouth and selective surface flow through the pore to the permeate side. The flux through the membrane is controlled by surface diffusivity of molecules adsorbed in the pores of the membrane. Surface diffusion coefficients have been reported in the literature to be 100-1000 times bulk diffusion coefficients (3). This allows one to prepare relatively thick membranes (1-10 micron) while maintaining a high flux through the membrane. Additional advantages of this characteristic are that (i) supports for coating the membrane are not required to have a very small pore size, significantly reducing the cost of the membrane support, (ii) membrane repair techniques are not required and (iii) adsorption occurs at very low partial pressures and hence separations can be accomplished at very low feed partial pressures. Thus, the SSF membrane is capable of operating at low feed pressures. The selectivity of the membrane is affected by the adsorption selectivity of the various species in the feed on the membrane surface, pore blockage caused by the adsorbed molecules, and the transport selectivity of the molecules through the membrane. Thus, molecules that are selectively adsorbed are

transported to the permeate side and the less-selectively adsorbed molecules are recovered on the non-permeate side, a schematic is shown in **Figure 1**. For separations of interest in this program -- recovery of hydrogen from waste streams containing H_2 and light hydrocarbons -- the permeate stream is enriched in hydrocarbons while the non-permeate stream is enriched in hydrogen. Because hydrogen is the desired product species, it is collected at close to the feed pressure. This has the advantage that product compression is either eliminated or reduced. This advantage is in direct contrast with conventional practical membranes, where H_2 would constitute the permeate stream recovered at a pressure significantly lower than the feed pressure (i.e.,> 150 psig).

2.3 SSF Membrane Concept Demonstration

The proof of concept for the SSF membrane was demonstrated by preparing the membrane on flat porous carbon sheets, the details of which have been reported elsewhere (4). The SSF membrane prepared on a porous sheet is a thin film multi-layer carbon membrane with controlled pore size, pore size distribution and surface chemistry. The membrane is obtained by pyrolyzing polyvinylidene chloride (PVDC) in an inert atmosphere at 600-1000 C. Up to 5 layers of carbon membrane are coated on the support to obtain the desired membrane performance. The heating and cooling rates are controlled during the firing process (4). The carbon membrane is additionally passivated at 350 C by reaction with oxygen so that the membrane does not change/age by ambient-condition reaction with water or oxygen. It was determined that the carbon membrane, coated on the porous carbon sheet, has an average pore size of ~5 A, with a narrow pore size distribution (maximum pore size < 10 A), and has surface oxygen functional groups on a large number of carbon sites as determined by x-ray photoelectron spectroscopy (XPS).

The SSF membranes in sheet form were tested with pure and mixed gases to demonstrate the concept of surface flow and pore blockage effects to increase the membrane selectivity for hydrocarbons over hydrogen (1,2). Several applications for the membrane have been developed, including recovery of hydrogen from hydrocarbons (5), increased production of hydrogen in hydrogen plants by integration of the SSF membrane into the process (5,6) and fractionation of hydrocarbons (7). Separation properties of the membrane were measured with a typical H_2/hydrocarbon (C_1-C_3's) off-gas mixture from a Fluid Catalytic Cracker (FCC) in a refinery. **Table 1** summarizes the performance definitions for pure and mixed gas testing. The results from mixed gas performance characterization for the flat sheet membrane are shown in **Figures 2-5**. The data show that (i) large fractions of C_2^+'s can be simultaneously permeated through the membrane while enriching the H_2 in the high pressure effluent, (ii) the rejection of the permeate is inversely related to the recovery of hydrogen, and (iii) the membrane area required for separation increases at higher hydrocarbon rejections (i.e., lower H_2 recovery).

SEPARATION MECHANISM IN SELECTIVE SURFACE FLOW MEMBRANES

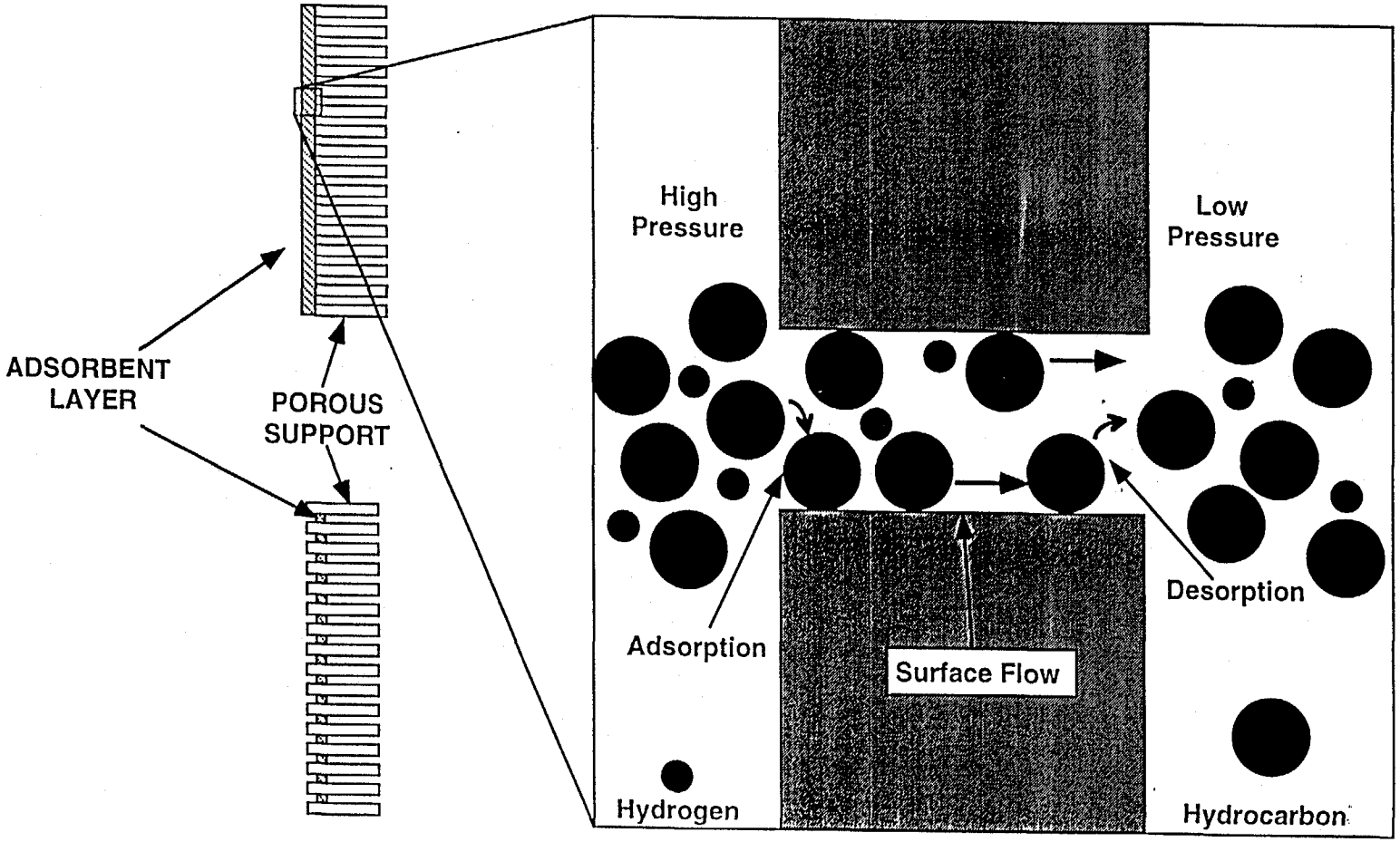
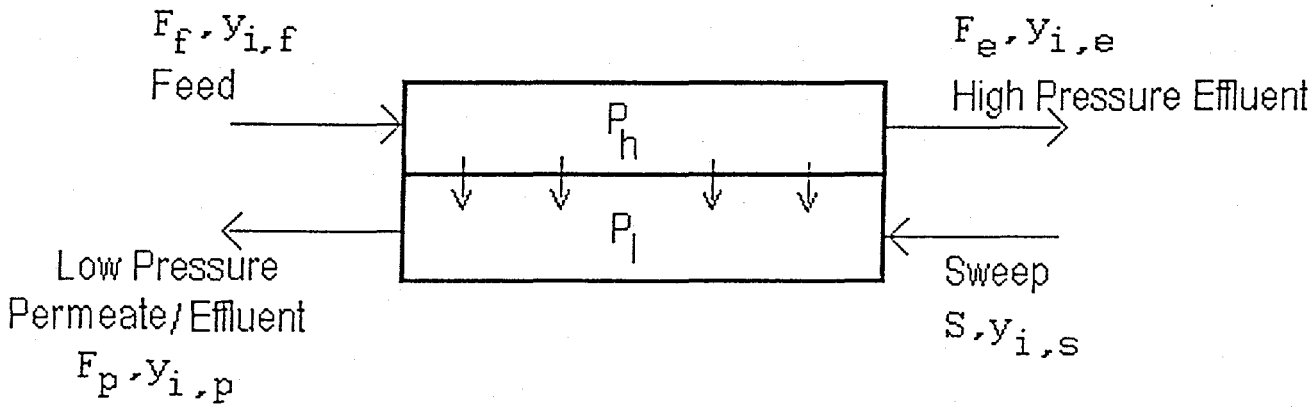


Figure 1. Separation Mechanism in SSF Membranes

TABLE 1

SSF MEMBRANE PERFORMANCE DEFINITIONS



Definitions :

F_f = feed flow rate ; $y_{i,f}$ = feed component mole fractions
F_e = high pressure effluent flow rate; $y_{i,e}$= high pressure effluent component mole fractions
F_p = permeate flow rate; $y_{i,p}$ = permeate component mole fractions
S = sweep flow rate; $y_{i,s}$ = sweep component mole fractions

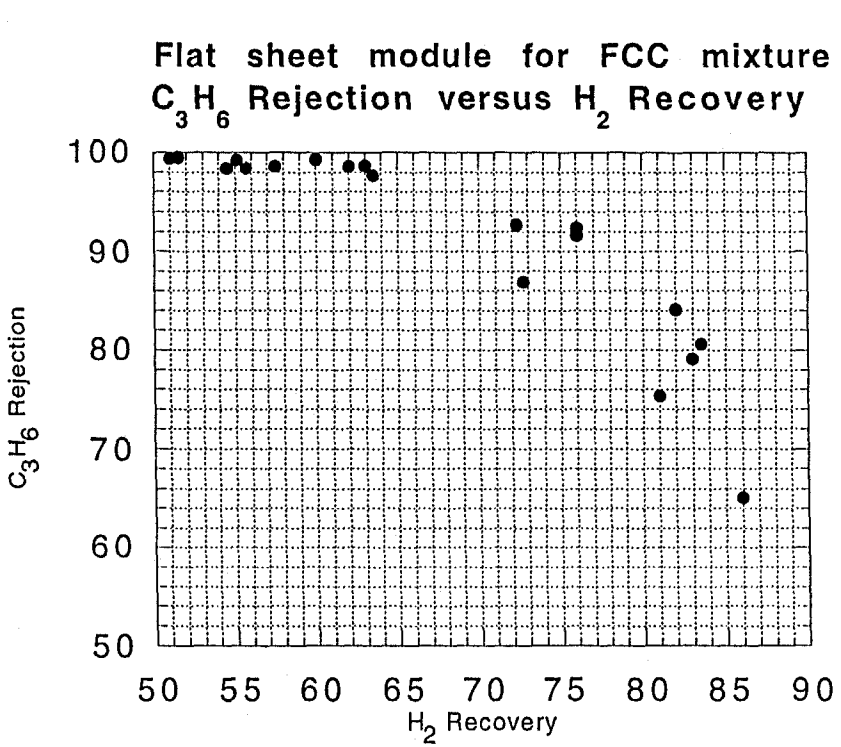
Recovery of component i = $(F_e \cdot y_{i,e})/(F_f \cdot y_{i,f})$
Rejection of component i = 1- $(F_e \cdot y_{i,e})/(F_f \cdot y_{i,f}) = (F_p \cdot y_{i,p})/(F_f \cdot y_{i,f})$

Flux = J = (P/l). A. Δp

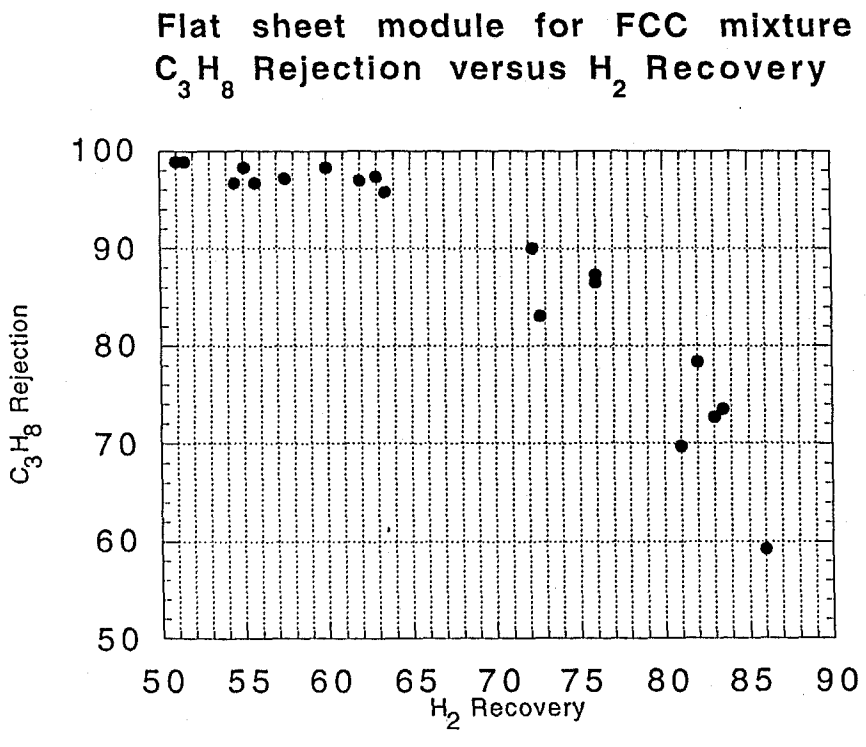
where P = permeability for specific gas, $cm^3.cm/s.cm^2.cm$ Hg
l = membrane thickness, cm
A = membrane area, cm^2
Δp = pressure drop across membrane = $(P_h - P_l)$, cm Hg
Permeance = P/l, $cm^3/s.cm^2.cm$ Hg

The permeance for a gas can be calculated from a pure gas test or from a mixed gas test

A/F = (membrane area)/(feed flow rate) , ft^2/lbmol/hr
= this is a function of the recovery or rejection of a specific component through the membrane

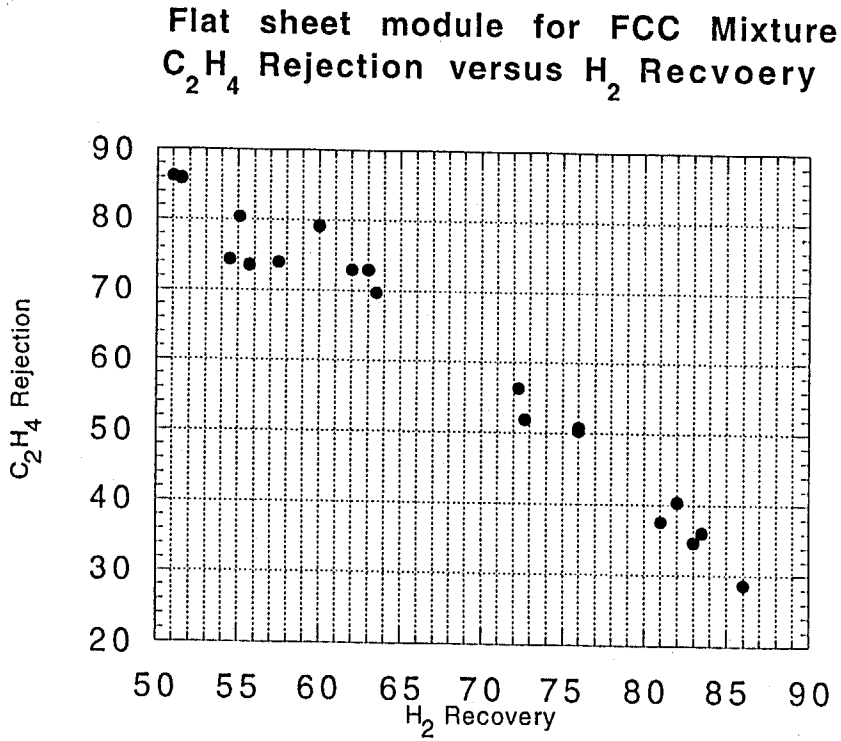


(a)

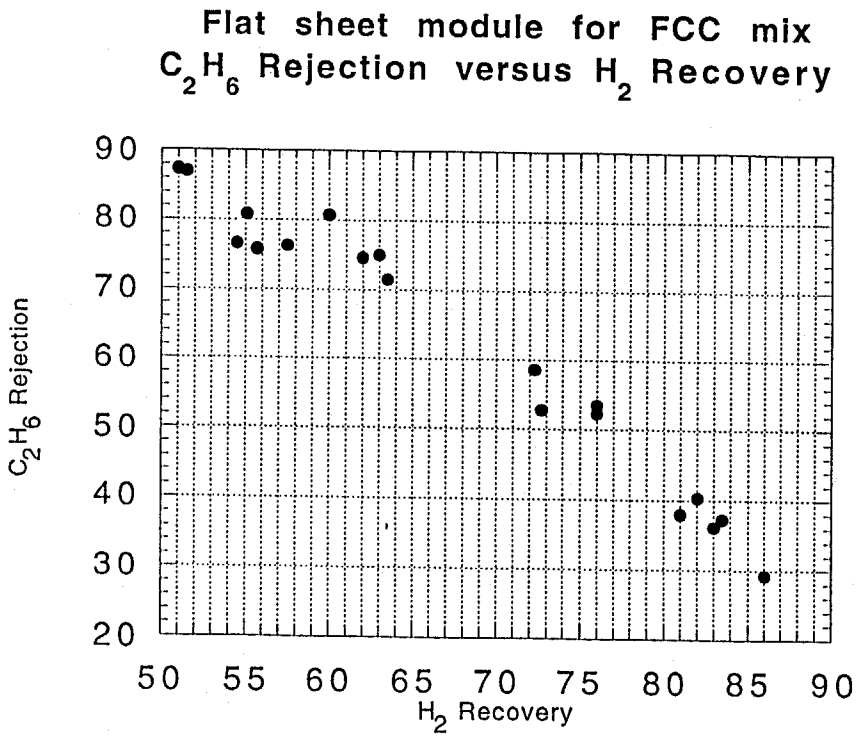


(b)

Figure 2. H_2 Recovery vs Propylene (a) and Propane (b) Rejections for 5-layer Sheet SSF Membrane



(a)



(b)

Figure 3. H_2 Recovery vs Ethylene (a) and Ethane (b) Rejections for 5-layer Sheet SSF Membrane

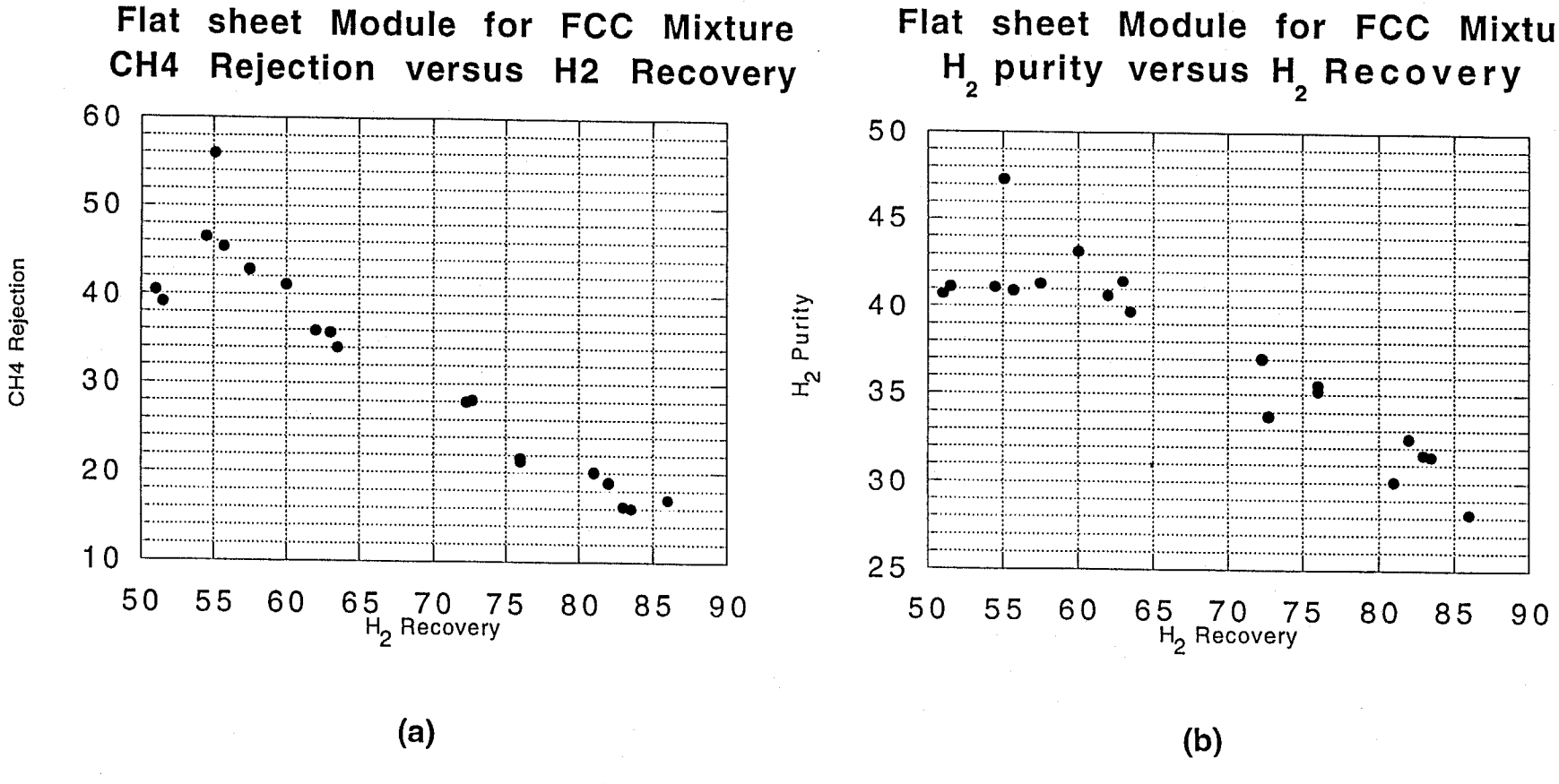


Figure 4. H_2 Recovery vs Methane Rejection (a) and H_2 Purity in High Pressure Effluent for 5-layer Sheet SSF Membrane

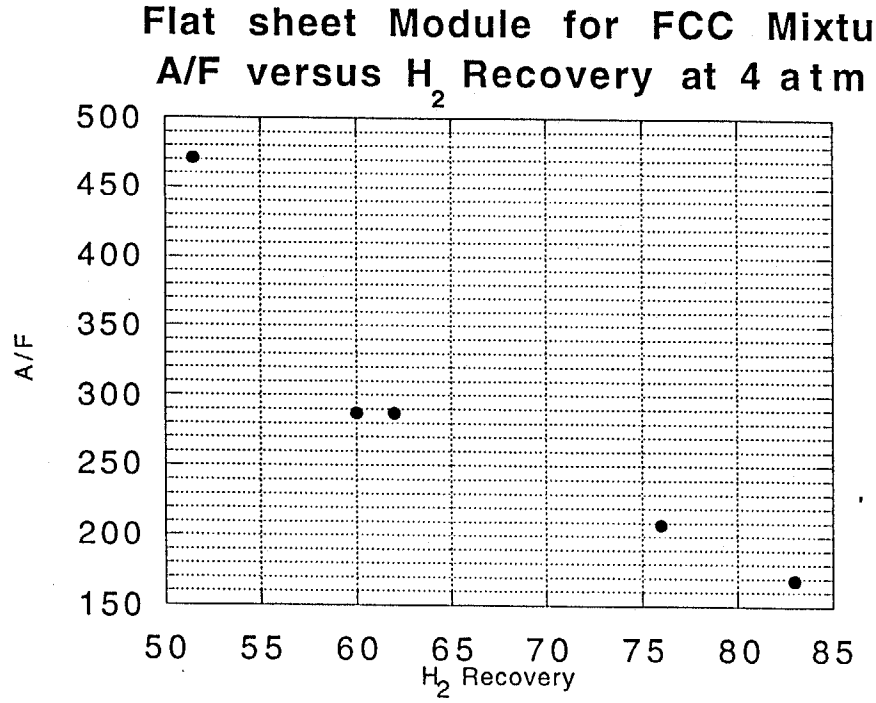


Figure 5. H_2 Recovery vs A/F for 5-layer Sheet SSF Membrane at 4 atm Feed Pressure