NOVEL SELECTIVE SURFACE FLOW (SSF^{TM}) MEMBRANES FOR THE RECOVERY OF HYDROGEN FROM WASTE GAS STREAMS

Phase I : Exploratory Development

Final Report

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PREFACE

This report documents Phase I, Exploratory Development, which was performed over the period April 1993 through October 1994. It is the first phase of a four phase project for the development of Selective Surface Flow (SSF^{TM}) membranes for the recovery of hydrogen from off-gas streams from various chemical/refinery operations.

In Phase I of the work, the architecture of the membrane and the separation device have been defined and demonstrated. The system consists of a shell-and-tube separator in which the gas to be separated is fed to the tube side, the product is collected as the high pressure effluent and the permeate constitutes the waste/fuel stream. Each tube, which has the membrane coated on the interior surface, does the separation in the system. The tube preparation, tube characteristics, membrane preparation and membrane separation characteristics were developed in this work. It was demonstrated that the separation characteristics vastly exceed those set as the benchmark for this work. A multi-tube separator device containing 1 ft^2 of membrane area was built and tested. The engineering data were used for design of a process for hydrogen recovery from a fluid catalytic cracker (FCC) off-gas stream. First-pass economics demonstrated that the overall cost for hydrogen production is reduced by 35% vs on-purpose production of hydrogen by steam-methane reforming. The hydrogen recovery process using the SSF membrane results in at least 15% energy reduction and a significant decrease in CO_2 and NO_x emissions.

In Phases II and III, the technology will be demonstrated in the field and scaled up to a semi-commercial unit.

This is a cost shared project between Air Products and Chemicals, Inc. and the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, under DOE Albuquerque Field Office Cooperative Agreement DE-FC04-93AL94461. Bruce Cranford and Charles Russomanno have been the Program Managers for the DOE Office of Industrial Technologies. Porter Grace and Ken Lucien have been the Project Managers for the DOE Albuquerque Operations Office. Frank Childs, the Project Technical Monitor for DOE, is on the staff of Scientech, Inc., Idaho Falls, ID.

For Air Products and Chemicals Inc., Madhu Anand is the Program Manager and Principal Investigator. Barry Halper is the Contracting Manager. Jim Yang is also a Principal Investigator for Phase I of the program. Additional technical contributors to the program are Beth Campion-Louie, Sheila Wirth and Sherri Lilienfeld. Shivaji Sircar and Madhukar Rao have been active consultants in this work.

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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
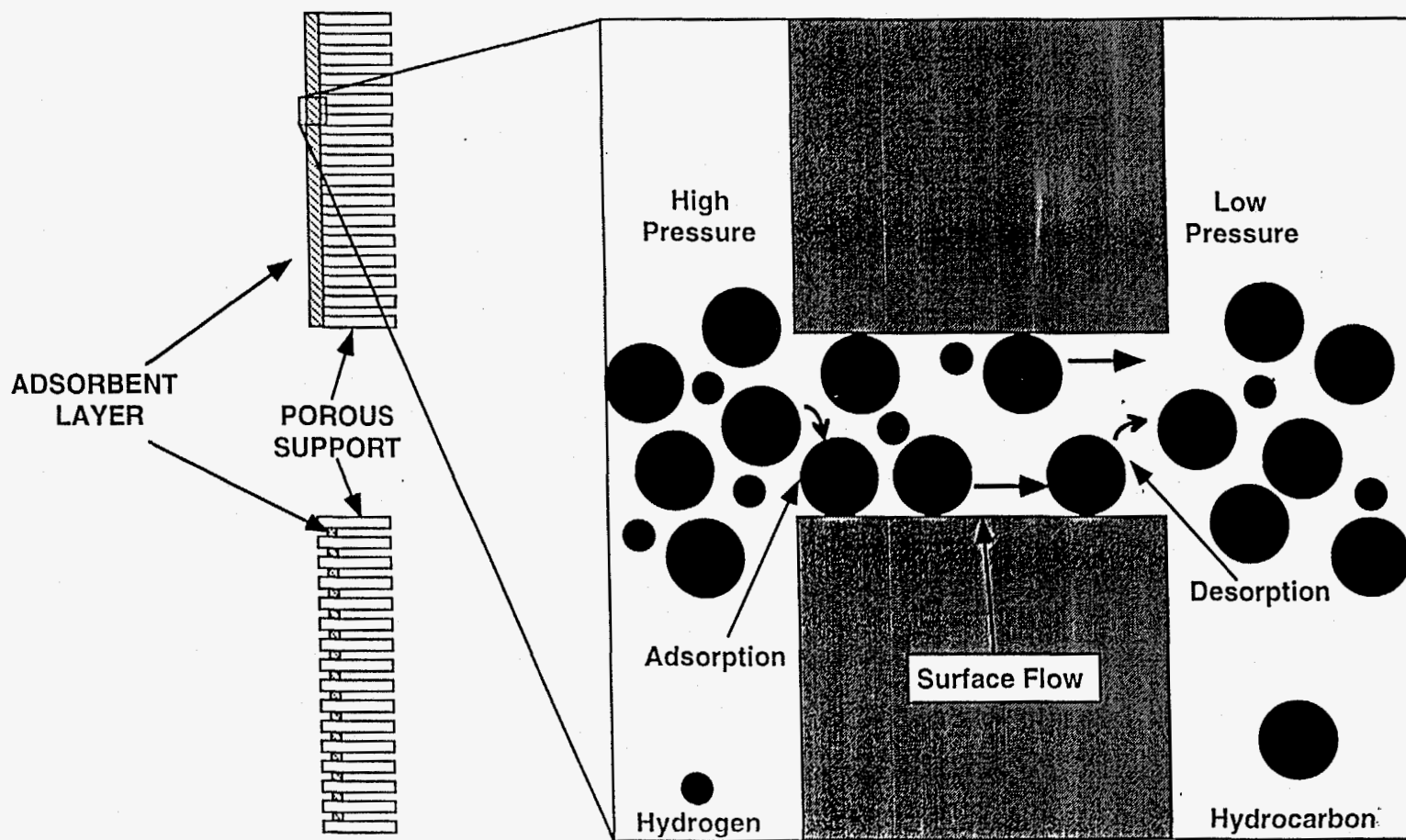
Figure 1. Separation Mechanism in SSF Membranes

TABLE 1

SSF MEMBRANE PERFORMANCE DEFINITIONS
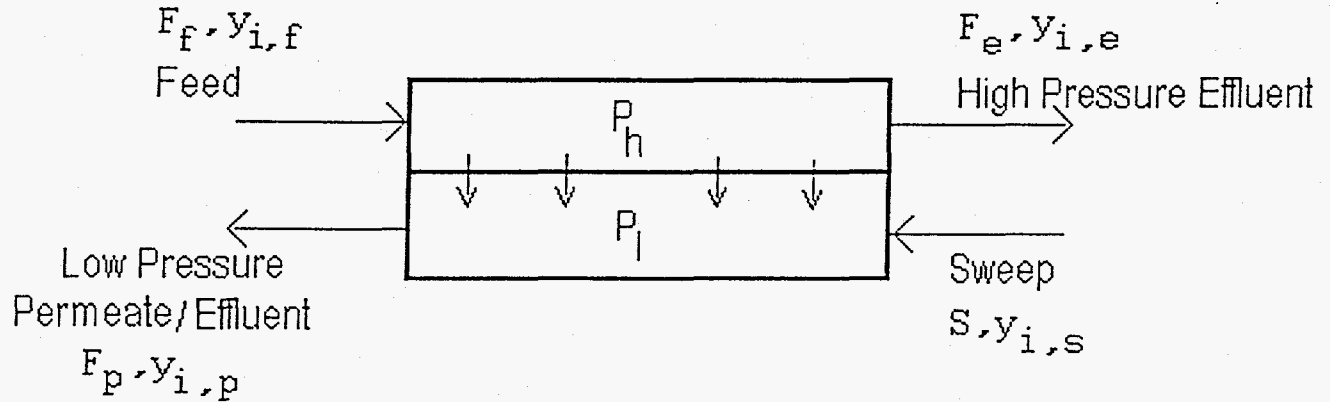
Definitions :

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 = $J = (P/l). A. \Delta p$

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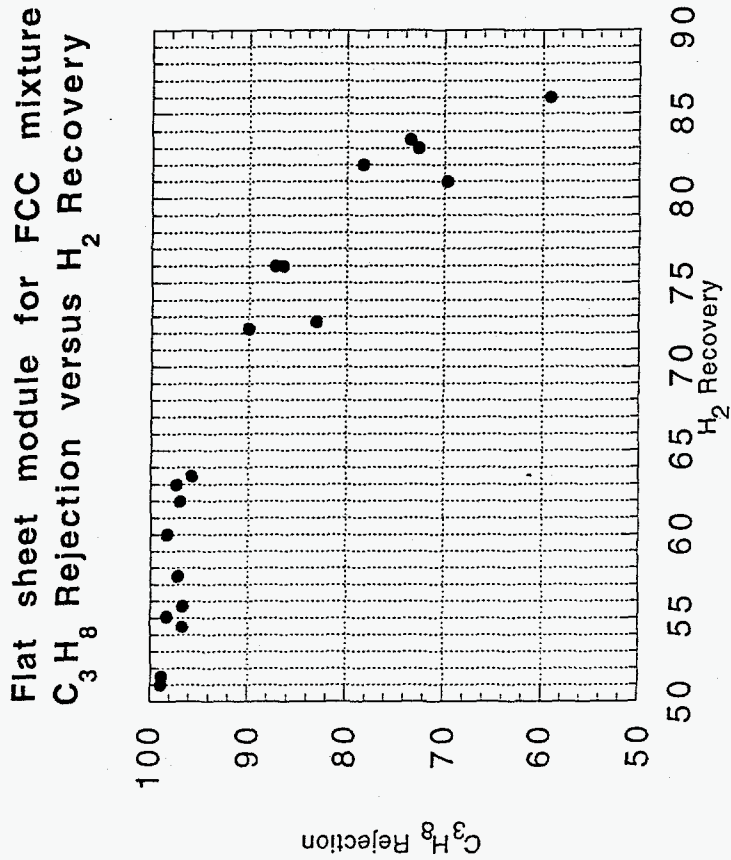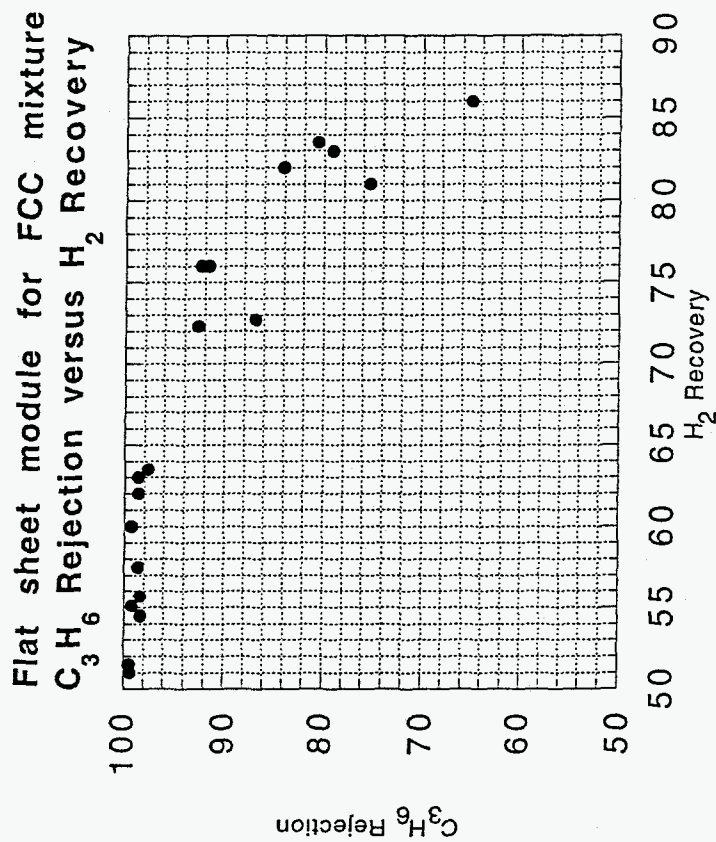
Figure 2. H_2 Recovery vs Propylene (a) and Propane (b) Rejections for 5-layer Sheet SSF Membrane

Flat sheet module for FCC Mixture
C_2H_4 Rejection versus H_2 Recvoery

C_2H_4 Rejection
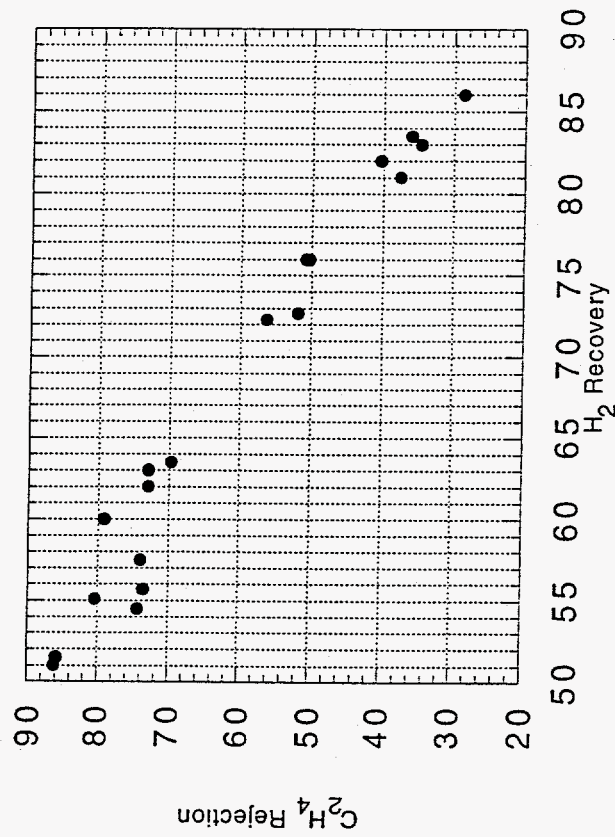
H_2 Recovery

(a)

Flat sheet module for FCC mix
C_2H_6 Rejection versus H_2 Recovery

C_2H_6 Rejection
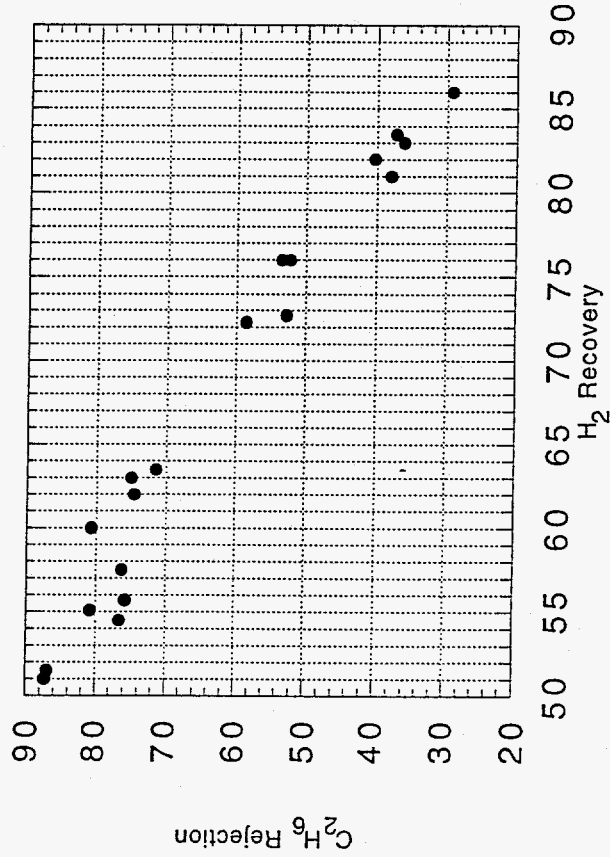
H_2 Recovery

(b)

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

3d
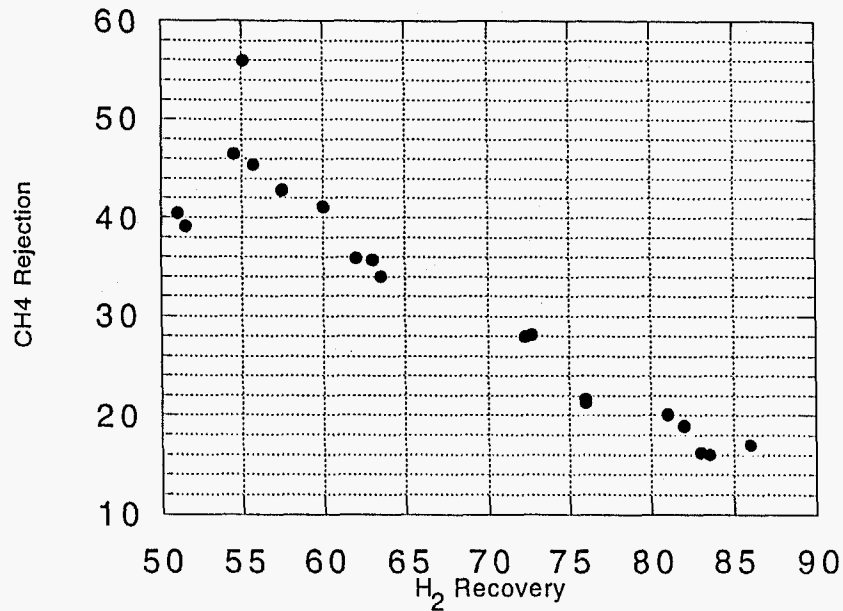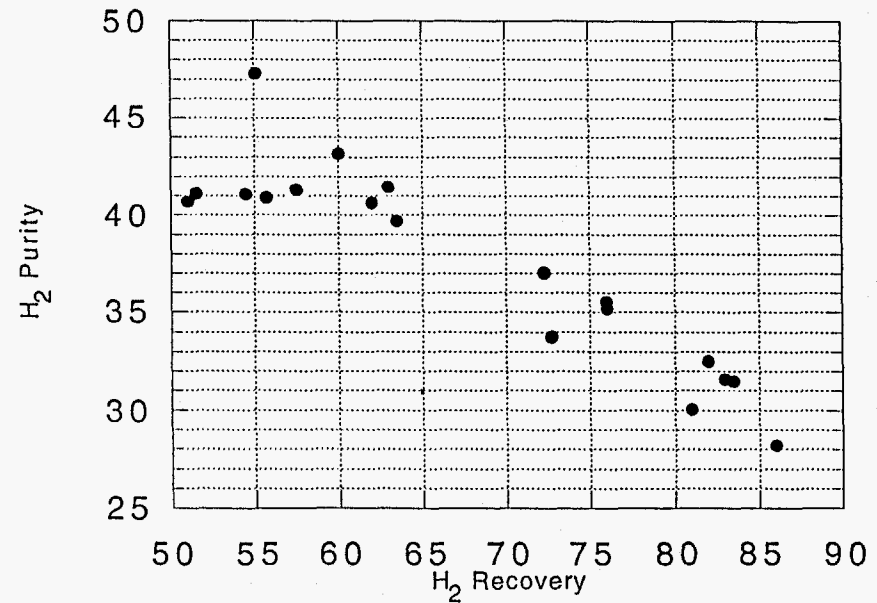
Figure 4. H_2 Recovery vs Methane Rejection (a) and H_2 Purity in High Pressure Effluent for 5-layer Sheet SSF Membrane

3e

Flat sheet Module for FCC Mixture
A/F versus H_2 Recovery at 4 atm
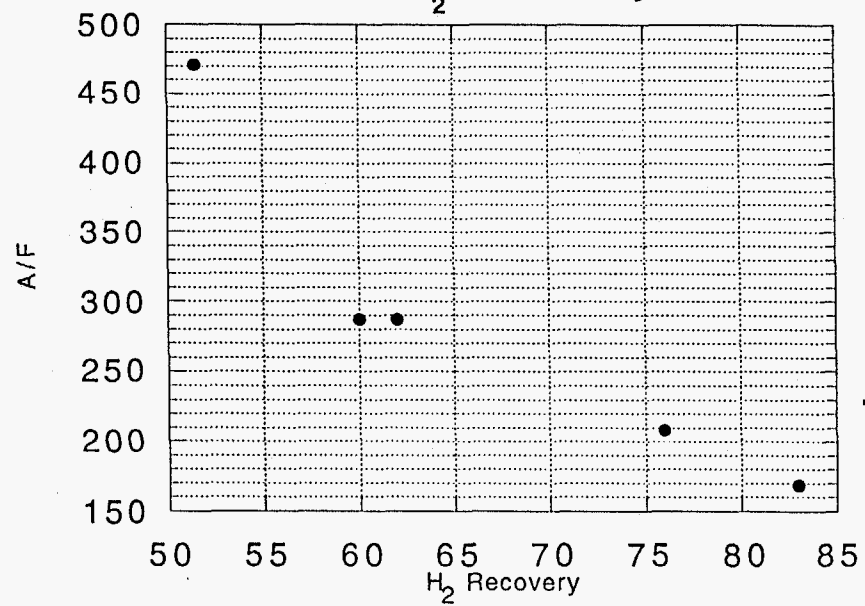
Figure 5. H_2 Recovery vs A/F for 5-layer Sheet SSF Membrane at 4 atm Feed Pressure

A multi-sheet module with about 0.5 ft^2 membrane area was prepared and tested continuously with a laboratory-blended FCC H_2/HC mixture (containing 20% H_2, 20% CH_4, 16% C_2's and 44% C_3's) over a six month period. No decrease in membrane performance was observed (1).

Thus, as a part of the proof of concept, it was demonstrated that the SSF membrane can be reproduced on porous graphite sheets and that these membranes are stable with continued use with a clean H_2/HC mixture.

## 3.0 MEMBRANE FABRICATION SCALE-UP

The objectives of the membrane fabrication scale-up were to develop the following:
(i) A support for coating membranes that is scalable, commercial and cost effective,
(ii) A membrane preparation method that is reproducible, scalable and cost effective,
(iii) A 1 ft^2 area membrane for demonstration of scalability and field testing,
(iv) Membrane performance data for process engineering, design, and first pass economics.
The following sections discuss the results for each of these objectives.

3.1 Substrate for Coating Membrane

The list of requirements for a scalable support for the SSF membrane is shown in **Table 2**. Several different types of porous supports meet the requirements, including tubes, multi-channel structures and hollow fibers. **Table 3** summarizes the supports that were evaluated and also indicates the ones on which the SSF membranes could be coated successfully. In the evaluation of the various porous supports, the pore size, pore size distribution, porosity, coating thickness and multiple coatings were investigated. Some of the criteria listed in **Table 2** were developed based on the results from these screening evaluations. Based on the support cost and membrane performance, it was decided that the focus for detailed studies would be on ceramic tubes and monoliths with homogeneous structures. The concept of tailoring ceramic tubes for coating gas separation membranes is not widely practiced. Most researchers developing ceramic gas separation membranes have focused on coating commercial alumina tubes used in liquid microfiltration and ultrafiltration applications. These tubes are typically asymmetric structures with a large pore (~ 100 micron pore) α-alumina base, coated with multiple layers of γ-alumina coated from γ-alumina sols to prepare tubes with surface pores ranging from 40 A to 2000 A (e.g., Ref 8). Recently there have been some efforts in sol-gel coating of cordeirite monoliths (multi-cell structures) with γ-alumina for use of the structures as particulate and liquid filtration devices (9). The above supports are expensive -- typically $ 500-2,000/\text{ft}^2$ of membrane area -- and have not been used in gas separations because of large membrane area requirements and the corresponding large membrane capital costs. Thus, the development of a low cost (< $50/\text{ft}^2$) ceramic support for the SSF membrane is a critical factor in successfully scaling up this membrane.

TABLE 2

REQUIREMENTS FOR SSF MEMBRANE SUPPORT

1. Pore size 50 A to 7,000 A
2. Low surface roughness
3. Narrow pore size distribution - max pore size < 1.5 micron
4. Total Porosity > 20%, preferably about 40%
5. Stable in temperature range 500 C - 1000 C
6. Thermal expansion coefficient $5 - 10 \times 10^{-6}/°C$
7. Tube ends sealed to prevent by-pass flow through cross-section
8. Can tolerate heating and cooling rates of up to 20°C/min
9. Mechanical strength to withstand $\Delta p > 250$ psig
10. Materials can be carbon, alumina, cordeirite (and other ceramics), glass
11. Cost of support is low

TABLE 3

SUPPORTS EVALUATED FOR COATING SSF MEMBRANE

Support Type	Cost	Success
1. Porous carbon tubes with different pore sizes	H-M	P
2. Hollow porous carbon fibers	M	N
3. Asymmetric α-alumina tubes with different pore sizes	H	Y
4. Cordeirite and mullite tubes	L	Y
5. Multi-channel cordeirite structures coated with γ-alumina	M-L	I
6. α-Alumina tubes with homogeneous structures	L	Y
7. Porous glass tubes	H	N
8. Cordeirite and mullite homogeneous monoliths	L	O

H = High, M = Medium, L= low
P = Partial success
N = not successful
Y = successful
I = incomplete/not successful due to methods used
O = not evaluated

SSF membranes were prepared on alumina, mullite, cordeirite and carbon tubes with pore sizes varying from 0.2 to 5 microns. These tubes are homogeneous in structure and have the same pore size across the tube cross-section. It was determined that membranes with the desired separation properties could be prepared with multiple coats on supports with pores < 1.0 micron. It was also determined that a narrow pore size distribution was critical in preparing a membrane with target separation properties, and pores > ~1.5 micron were undesirable. It was very significantly determined that a membrane with target properties could be reproducibly prepared in a single coat on a ceramic support with a pore size of ~0.3 micron and a maximum pore size <1.0 micron. The total porosity in such supports is >20%. Thus, the outcome of the screening work was to focus on the development of the alumina tubes for optimization of the membrane properties.

3.2. Alumina Tubes for SSF Membranes

In the optimization of the alumina tubes, the following tube characteristics were varied : (i) porosity, (ii) strength, (iii) binder type (iv) alumina particle size (v) tube end finish. The concentrations of the alumina/binder/lubricant/water were not varied in these experiments. The variations in the porosity and strength were achieved by firing the green extruded ceramic tube at different temperatures. The alumina tubes were prepared at a variety of conditions by the tube supplier.

Table 4 shows the tube firing/fusion temperatures of the alumina tubes and the corresponding tube properties. To balance the porosity with the mechanical properties of the tubes, a tube firing temperature of 1430 C was selected with this specific particle size alumina. This alumina allowed one to prepare tubes with the desired pore size and a very narrow pore size distribution. It was noted that the tubes prepared at 1430 C were prone to chipping at tube ends. The problem of tube-end chipping was solved by rounding the tube ends after firing. **Table 4** also compares tubes prepared by using a solid binder vs a gel binder. The use of a solid binder resulted in the formation of pits on the tube surface when the binder volatilized from the surface (**Figure 6**). This resulted in membranes with defects. The problem was solved by replacing a solid binder with a gel binder which coated the surface of the alumina particles and distributed uniformly in the extrusion compound (**Figure 6**).

A smaller particle size alumina for preparing the tubes was also evaluated as shown in **Table 4**. Tubes with the smaller particle alumina could be fired at ~ 1200 C while having acceptable mechanical properties. This option was eliminated because of lower gas permeation through these tubes. However, with optimization, these tubes could be possible candidates for separation applications at higher membrane feed pressures.

TABLE 4

OPTIMIZATION OF THE STRUCTURE OF THE ALUMINA TUBES

Firing Temperature, C	Binder	Porosity* %	Pore size* μ	Pore* Volume,cc/g	Mechanical Strength
Tubes with larger particle size alumina :					
975	gel	41.0	0.369	0.192	weak/brittle
1200	gel	37.6	0.276	0.159	weak/brittle
1430	gel	27.5	0.274	0.093	strong/ends chip
1450	gel	26.4	0.290	0.090	strong/ends chip
1470	gel	23.3	0.227	0.073	strong
1550	gel	12.4	0.228	0.036	strong
975	solid	39.1	0.281	0.171	weak
1200	solid	37.2	0.306	0.155	weak
1500	solid	9.7	0.181	0.028	strong
Tubes with smaller particle size alumina :					
975	gel	40.8	0.092	0.183	strong/ends chip
1200	gel	33.4	0.092	0.130	strong
1550	gel	0.4	--	0.001	strong/dense

* Measured by mercury porosimetry

(b)

(a)
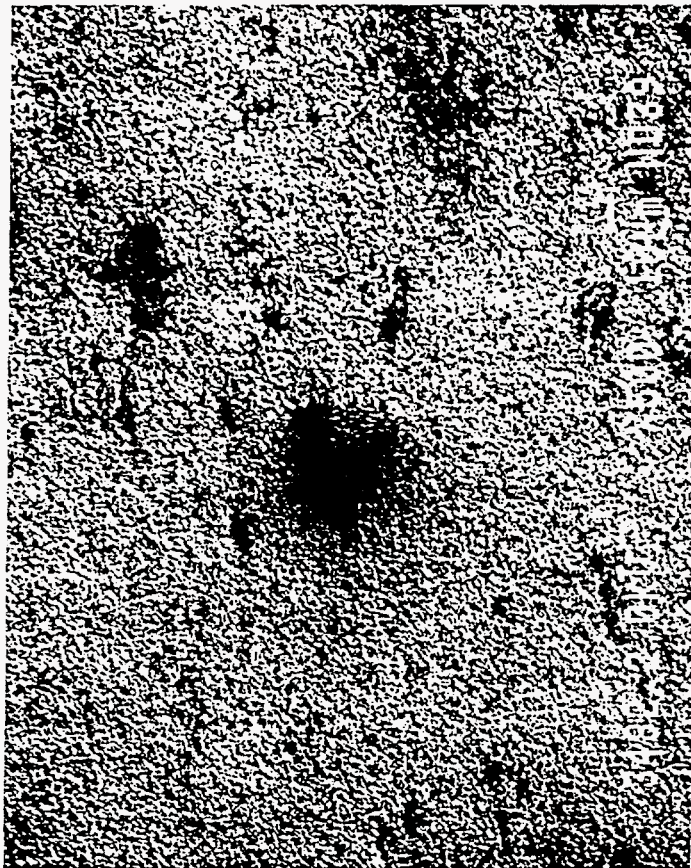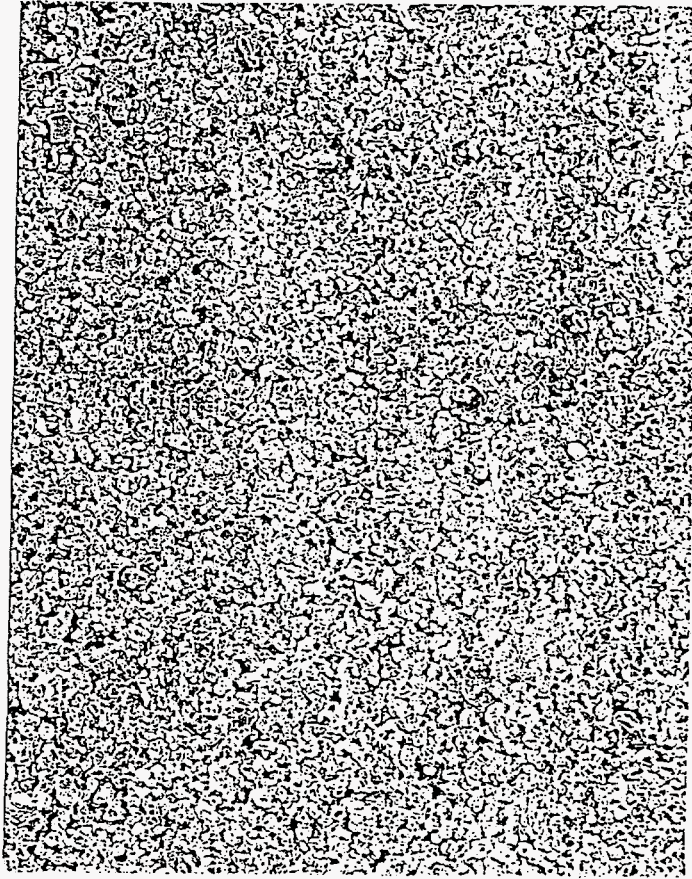
Figure 6. SEM Micrographs Showing Pits in Alumina Tubes due to Solid Binder (a), and the Absence of Pits with a Gel Binder (b)

5b

In addition, the tube edges were glazed with a silica/zirconia glass to prevent direct flow of gas through the tube ends. The tube interior is glossy and free of gross indentations, pits and streaks. Quantitative characterization of such defects in tube production has not been achieved yet.

Finally, the cost estimate provided by the supplier indicated that the tube cost would be within the Air Products set target.

3.3 Define Membrane Preparation Process

A membrane preparation process that coats the SSF membrane on the interior surface of the porous alumina tube was developed, the key steps for which are shown in **Table 5.** In the membrane preparation process, the tube is first cleaned with high pressure nitrogen to remove loose particles from the tube interior and is then conditioned at 100 C to remove most of the water in the larger pores. The membrane precursor, PVDC, is coated on the tube interior by a fill-and-drain sol-gel process in which the tube is filled with the emulsion, held for a fixed length of time and drained through a fixed size orifice (**Figure 7**). The PVDC sol is converted to a gel layer at the liquid-solid interface by capillary suction of the water into the membrane porosity. The coating thickness is primarily controlled by (i) the solids content in the emulsion, (ii) the tube porosity characteristics and (iii) the liquid hold time. After the emulsion is drained from the tube, the coating is dried by holding the tube vertically. Slow convective drying occurs in this step. The PVDC coating is then tested for its average thickness by measurement of the mass of polymer deposited. The quality of the tube coating is evaluated by measuring the permeation of helium or nitrogen through the coating, the equipment for which is shown in **Figure 8**. A good coating ensures a very low permeation (< 20 scc/s.cm2.cm.Hg) of helium through the membrane. Tubes with acceptable PVDC coating are pyrolyzed at 600 -1000 C in an inert atmosphere. During the cooling cycle, the membrane is passivated by reaction with oxygen at 350 C. This prevents membrane degradation with time which would otherwise occur by slow reaction with ambient moisture and air. A glossy, uniform thin layer membrane that adheres extremely well to the alumina support is obtained by this preparation technique. The details of the key steps identified in **Table 5** are discussed below.

3.3.1 Tube Conditioning

Three different techniques for removing loose particles on the tube interior surface were evaluated: (i) blowing with high velocity air/nitrogen, (ii) ultra-sonic cleaning with distilled water and (iii) ultra-sonic cleaning with isopropanol. No significant differences in PVDC coating quality between the different cleaning methods (other than no cleaning) were observed, as shown in **Table 6**. Blowing with high velocity nitrogen was adopted as the standard procedure because of the short operation time.

Tube pre-drying at 100 C was adopted as a standard to ensure that all the tubes were dry to the same extent. Varying moisture levels in the porosity would vary the capillary suction in the tube and hence produce varying coating thicknesses.

TABLE 5

MEMBRANE PREPARATION PROCESS STEPS

Coating of Alumina Tubes

Tube Conditioning :

1. Tube cleaning
2. Tube pre-conditioning

Emulsion Preparation :

1. Diluted Emulsion
2. Filtration at point of use

PVDC Coating :

1. Tube filling with emulsion and drainage
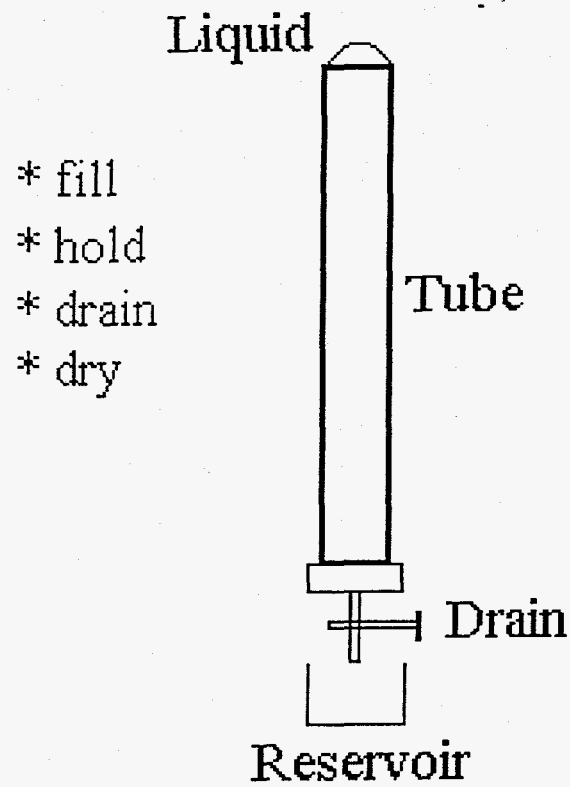2. Drying
3. Test quality of PVDC coating

Preparation of Carbon Membrane

Pyrolysis of PVDC :

1. Heating and cooling cycle
2. Test SSF Membrane

FIGURE 7

COATING OF TUBE INTERIOR

Liquid

* fill
* hold
* drain
* dry

Tube

Drain

Reservoir

FIGURE 8

MODULE FOR TEST OF PURE AND MIXED GAS PERMEATION

(RECOVERY)
high pressure effluent

low pressure
sweep gas

tubular
membrane

housing

low pressure

permeate

(REJECTION)

Feed gas in
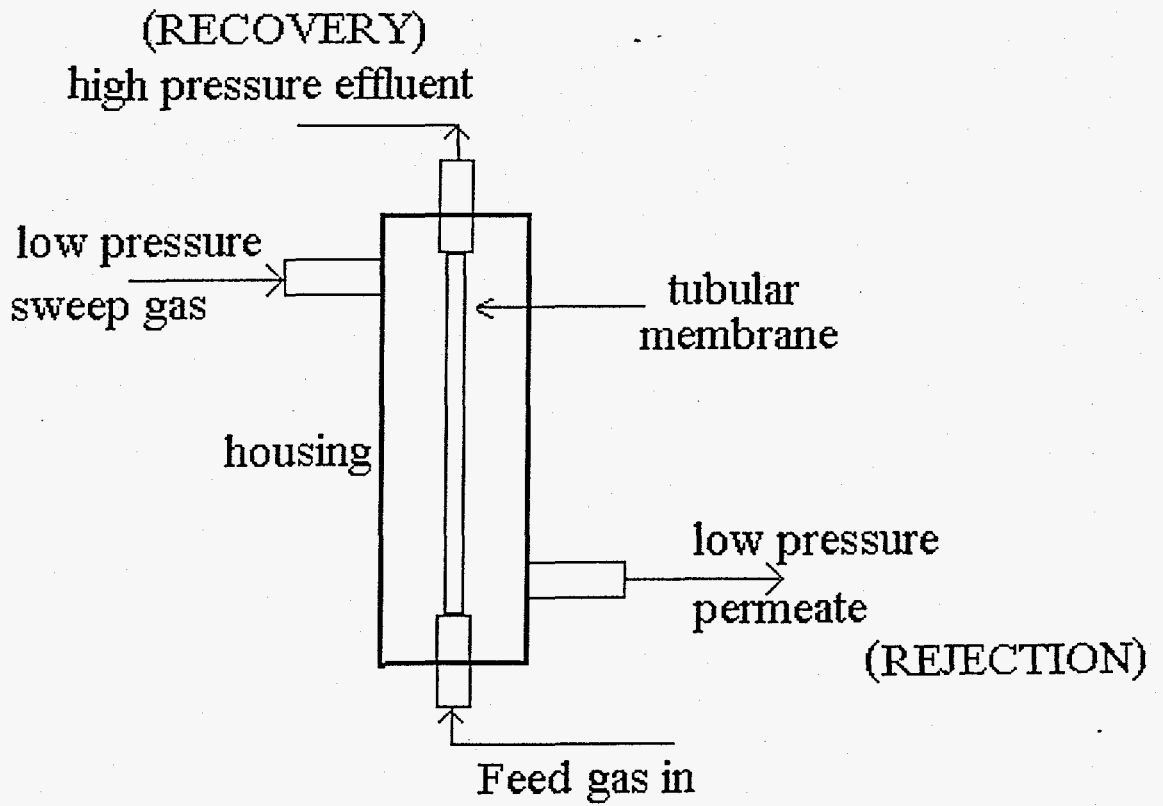
TABLE 6

EFFECT OF TUBE PRE-CLEANING ON PVDC COATING QUALITY

Coatings from 3.4% emulsion with different lots of alumina tubes

Pre-cleaning	PVDC Coating Thickness micron	Helium Permeance $scc/s.cm^2.cm\ Hg \times 10^{-5}$
As-is	6.5	350-30*
High Velocity N_2	6.1	19
Water Wash	6.6	22
High Velocity N_2	12.4	9.8
Iso-propanol Wash	11.7	10.2

Coating thicknesses and He permeances averages of several samples

Coating thickness calculated from weight of coating on tube and a specific gravity of 2.6 g/cc

*Permeances were highly variable without precleaning

3.3.2 Emulsion Preparation

The PVDC used for coating is a water-based emulsion (Daran 8600C, Hampshire Chemical Company, MA). The as-received emulsion contains 51% solids which is diluted to <10% solids with distilled and de-ionized water. The diluted emulsion is prepared by low intensity mixing of the as-received emulsion and water at room temperature. The emulsion is stored for < 1day and is used once-through (i.e., no reuse after drainage from the tube).

The diluted emulsion is filtered at the point of use through a combination of 5 μ and 2 μ filters in series and used directly for coating. This ensures that the largest contaminant particle is smaller than the membrane coating thickness. The filters are replaced once they are clogged.

3.3.3 PVDC Coating

The PVDC coating (precursor to the carbonized membrane) is done by filling the tube with the filtered diluted emulsion, holding for a fixed length of time and then gravity draining. The significant variables affecting the coating thickness are : (i) solids content in the emulsion, (ii) porosity in the tube and (iii) hold time prior to drainage. The specific effects of these variables were evaluated to obtain a defect-free membrane in a single coating as opposed to previous demonstration of the sheet membrane by multiple coats of the carbon film.

Table 7 shows the effect of emulsion solids content on the coating thickness. The data show that the coating thickness increases almost linearly with increased solids content in the emulsion in the range of emulsion solids content investigated. In addition, it has been observed that the coating thickness is strongly affected by the total porosity in the tube. **Table 8** shows the effect of porosity (at the same pore size) on the coating thickness. The coating thickness changes highly non-linearly with the porosity in the tube, with larger PVDC coating thickness on a more porous tube. The coating thickness is controlled by the capillary suction of the water into the tube and the formation of a PVDC gel layer on the tube interior. The fact that capillary effects are significant is shown in **Table 9,** which shows the effect of pre-filling the tube porosity with water prior to coating. The coating thickness is reduced by an order of magnitude by the elimination of water removal capability from the emulsion sol by capillary suction in the alumina tube porosity.

The wall thickness of the tube also changes the total capillary volume and hence impacts the coating thickness. **Table 10** shows the effect of tube wall thickness on coating thickness for tubes with the same pore size and porosity. The data expectedly show that the thicker wall tube causes the coating thickness to be greater (note : a thicker wall has a greater total pore volume available and hence more of the dilute emulsion can achieve a solids content which causes the polymer to gel). Hence, once the wall

TABLE 7

EFFECT OF SOLIDS CONTENT IN EMULSION ON THE PVDC COATING

Data with Lot 2 and 3 tubes

Solids Content %	Weight PVDC coating, g	PVDC thickness micron	Helium Permeance scc/s.cm^2.cm Hg x 10^{-5}
2.5	0.0346	3.0	103
3.0	0.0770	6.5	49
3.4	0.0820	7.0	35
6.8	0.1655	14.1	15
13.8	0.3946	33.7	6

TABLE 8

EFFECT OF TUBE POROSITY ON COATING THICKNESS

BASIS :

Tubes with varying porosity but constant pore size
Coating form 3.4 % emulsion

Tube Porosity %	Pore size micron	PVDC Coating Thickness micron
22	0.256	5.1
24	0.251	8.0
27.5	0.274	11.1

TABLE 9

CAPILLARY EFFECTS ON PVDC COATING THICKNESS

All coatings on lot 2 and 3 Tubes

Solids in Emulsion %	Weight PVDC Coating, g	
	Dry Tube	Tube wall filled with Water
3.4	0.0820	0.008
6.8	0.1655	0.015
13.8	0.3946	0.041

TABLE 10

EFFECT OF TUBE WALL THICKNESS ON COATING THICKNESS

Lot 4 and 5 tubes
All coatings from 3.4% emulsion

Wall thickness	Tube Porosity, %	Pore size, μ	Coating thickness, μ
2.0 mm	26.2	0.275	12.2
1.5 mm	27.5	0.274	8.8

thickness is specified based on mechanical strength requirements, the wall thickness needs to be controlled to obtain a consistent product.

Table 11 shows the effect of hold time of the emulsion in the tube on the PVDC coating thickness. The data show that the hold time is not a strong variable with this pore size and porosity tube, though there is a small increase in the coating thickness after the emulsion is held in the tube for 15 minutes. This observation is supported by the strong effect of initial capillary suction in rapidly forming a polymer gel layer which controls the coating thickness. Two minutes hold time was selected for coating operations. It may be possible to reduce this in manufacturing operation where the coating operation would be a mechanical process rather than the current manual process.

A typical PVDC coating on the alumina tube is shown in the SEM micrograph in **Figure 9**. The coating is about 18 micron thick and uniform under the specific preparation conditions used.

In summary, the data show that the PVDC coating thickness and quality on the porous support can be controlled by several process as well as tube related variables. The optimal coating for the SSF membrane is obtained by a combination of these variables.

3.3.4 Pyrolysis of PVDC

The SSF membrane is prepared by the pyrolysis of PVDC at an elevated temperature in an inert environment. **Figure 10** shows a thermogravimetric analysis (TGA) trace of the decomposition of PVDC coated on an alumina tube in a nitrogen environment. The pyrolysis occurs in three different stages as shown in **Figure 10**. The bulk of the dehydrohalogenation occurs from 120 C to about 250 C. A second weight loss occurs around 290 C, and pyrolysis is complete at 550 C. The mass loss accompanying pyrolysis is 75% (note : mass loss shown in **Figure 10** includes the mass of the alumina support and hence does not show the mass loss from the film alone). It has been determined that the secondary mass loss peaks are critical in the final pore size control since membranes pyrolyzed at intermediate temperatures do not have the desired gas separation properties. The mass loss during pyrolysis shrinks the thickness of the film. For example, an 18 μ PVDC results in a carbon membrane with a thickness of ~4 μ **(Figure 11)**. No significant difference in membrane separation properties was observed in the pyrolysis temperature range of 600 C-1000 C for membranes prepared on tubes. 600 C was chosen as the temperature for pyrolysis.

An initial objective was to determine the minimum PVDC coating thickness required to produce a uniform defect-free carbonized membrane film on the alumina support in a single coating. PVDC coatings were prepared from emulsions with varying solids content and pyrolyzed at 600 C. The following observations and conclusions were made from these experiments:
(i) Smooth, highly glossy carbon coatings are obtained when the PVDC coating thickness is < ~15 μ **(Figure 12)**.

TABLE 11

EFFECT OF HOLD TIME ON COATING THICKNESS

All coatings done on lot 2 and 3 tubes with 3.4% emulsion

Hold Time	Weight PVDC, g	Coating Thickness, μ
1 min	0.0869	7.4
2 min	0.0820	7.0
15 min	0.1018	8.7
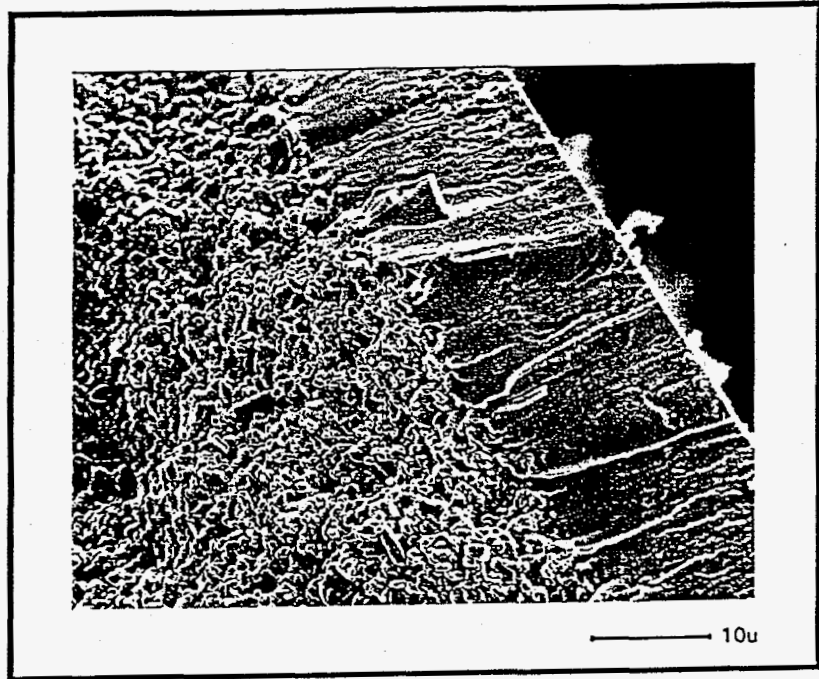
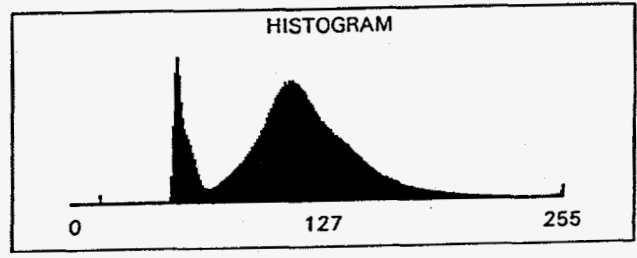| Title PVDC Alumina 14006-19-3 MA1932 | Date 05-12-94 | Time 14:22 |
| Comment cross-section area 2 | | |
| Mag X2,000   kV 5   WD 10mm | Spot 6 | Scan P3 |

HISTOGRAM

0   127   255

Figure 9.   SEM Showing Uniform PVDC Coating on Alumina Tube
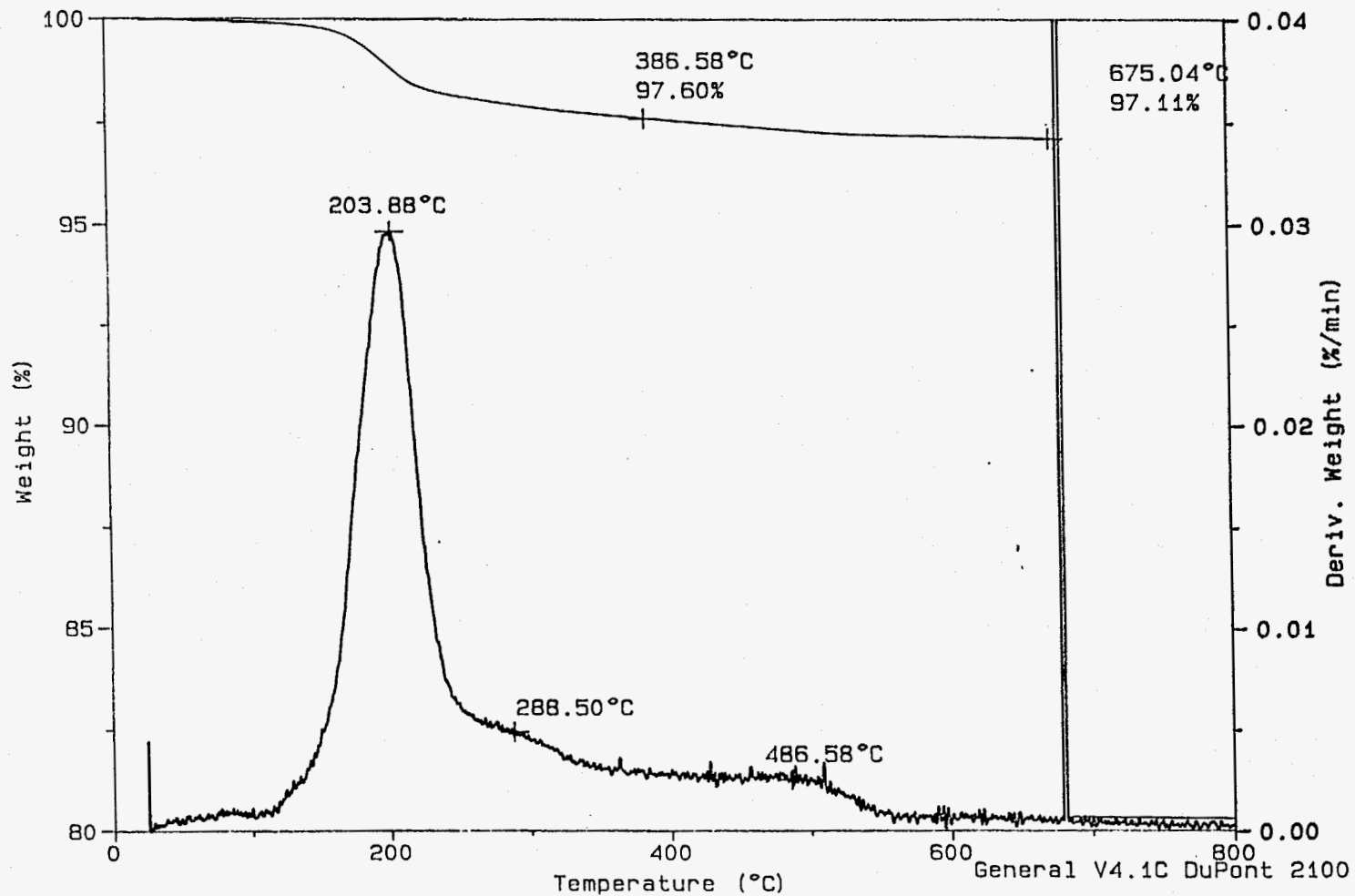
Figure 10. Thermogravimetric Analysis (TGA) of PVDC Coated on Alumina Tube. Note the Various Stages of Mass Loss upto 600 C

(b)

(a)
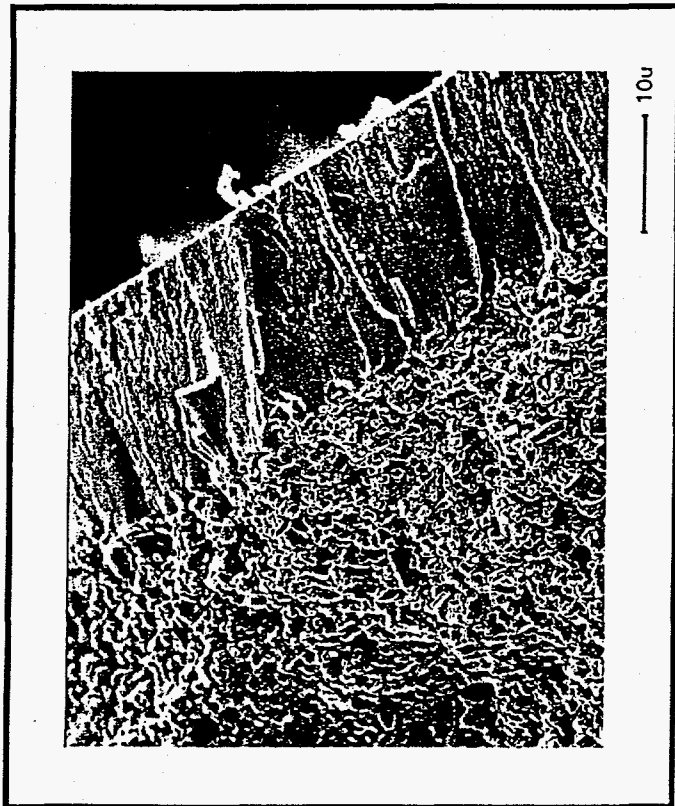
Figure 11. SEM of PVDC (a) and Carbon (b) Coatings on Alumina

8d
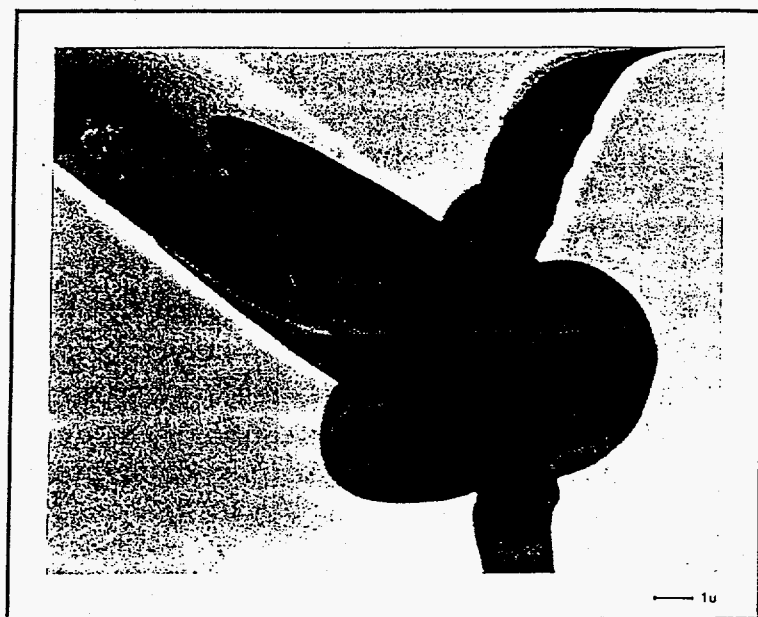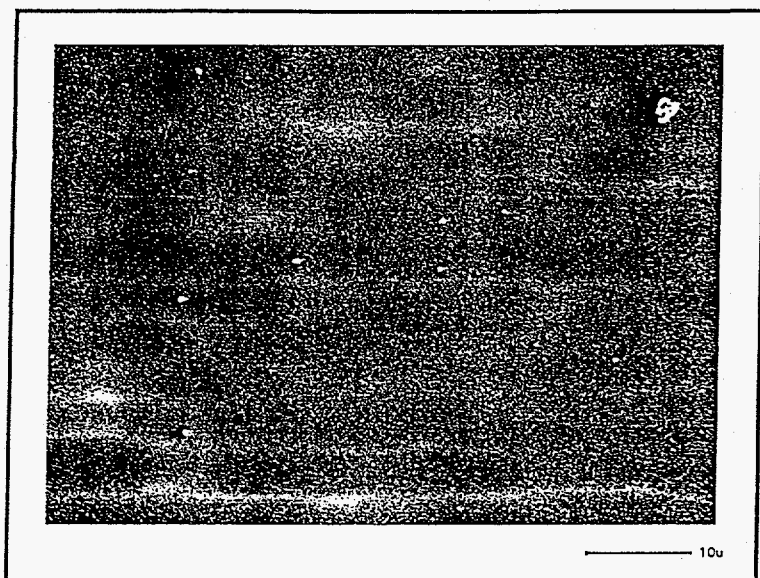
Title 14006-51-5 coated tube Date 02-08-95 Time 14:03
Comment good area MA5151
Mag X2,000 kV 2.0 WD 13mm Spot 7 Scan P3

(a)

Title C/alumina post-t 14006-19-6 Date 05-13-94 Time 14:42
Comment inner bore, MA1963
Mag X7,000 kV 5 WD 13mm Spot 5 Scan P3

(b)

(c)
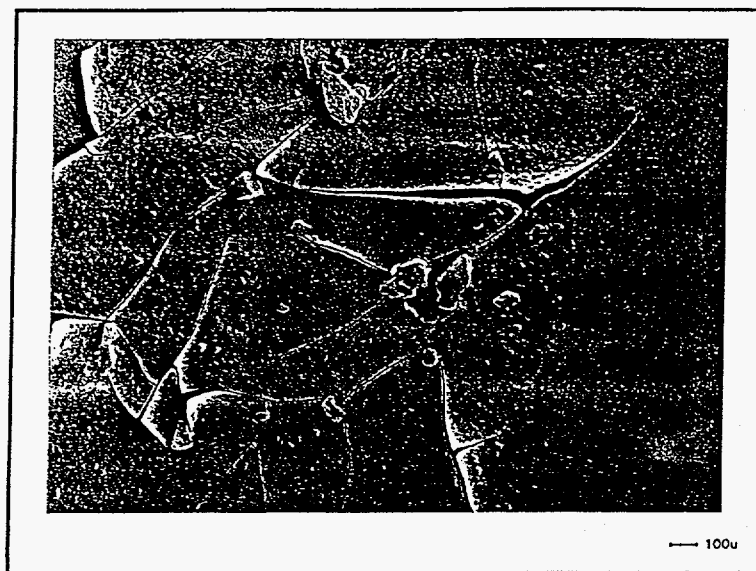
Title 14006-51-4 coated tube Date 02-08-95 Time 13:57
Comment defect area MA5146
Mag X50 kV 2.0 WD 13mm Spot 7 Scan P3

Figure 12. SEMs Showing (a) Smooth Membrane Surface, (b) Bubble
in Thick Membrane and (c) Multiple Cracks on Membrane.
The cracks and bubbles impart the membrane a matte appearance

8e

9

(ii) Bubble formation occurs in the carbon membrane if the PVDC film thickness is >~15 μ (**Figure 12**). The bubbles cause "local roughness", giving the tube interior surface a matte appearance.

(iii) Local variations in thickness can be induced by porosity variations and tube imperfections (e.g., pits), thus leading to gross local defects (e.g,. delamination, bubbles).

(iv) Batch-to-batch variations in tube porosity result in SSF membranes with variations in thickness if the PVDC is coated from an emulsion with a constant solids content.

(v) **Figures 13 and 14** show the variation in carbon coating thickness along the tube length and circumference as observed by SEM. There is some variation in the thickness along the tube circumference at the top, but not along the length for this particular tube. Local variations in tube porosity are likely responsible for this variation. Improvement in uniformity may allow one to reduce the membrane thickness.

To successfully prepare a membrane, a uniform and defect-free coating with the desired separation properties is prepared by judiciously choosing the conditions described in the above membrane preparation steps.

The as-is prepared SSF membrane on the alumina tube consists of nascent carbon, which can react slowly with atmospheric air or water. A membrane passivation step that allows controlled oxidation of the carbon membrane was developed on carbon sheets (10) and transferred to tubes. This step involves introducing air into the pyrolysis furnace at 350 C and exposing the membrane to air for a short period, followed by cooling in nitrogen. The SSF membrane prepared on the tubular support was treated in air at 350 C for various times and the mixed gas performance evaluated . The propylene rejection and the A/F at different hydrogen recoveries is shown in **Figures 15 and 16** for different passivation times. The data indicate that the the membrane performance deteriorates with 120 and 180 min of treatment. The results between 0 and 60 min treatment were indistinguishable. A thirty minute treatment in air was chosen as the standard passivation condition.

## 3.4 Reproducibility of SSF Membrane Preparation

After the alumina tube preparation technique was improved with the tube supplier so that tubes with consistent properties were obtained, the reproducibilty of the SSF membrane preparation technique was evaluated using a single batch of alumina tubes. **Tables 12 and 13** show results of mass/thickness of PVDC coating, helium permeance with PVDC coated tubes, pyrolyzed membrane thickness and the permeance of helium and carbon dioxide through the carbonized membrane for 65 tubes. The data show that the SSF membrane preparation on these tubes is reproducible. The variabilities in the PVDC average coating thickness and He permeance are low; the variations in carbon coating thickness and pure gas He and CO_2 permeances through the SSF membrane are also low. Pure gas permeation measurement with He and CO_2 though the SSF membrane is a good screening tool to determine if the pores in the membrane are in the desired size range. In separations by sieving and Knudsen mechanisms, pure He permeance is greater than pure CO_2 permeance. However, in the selected surface flow regime, the permeation
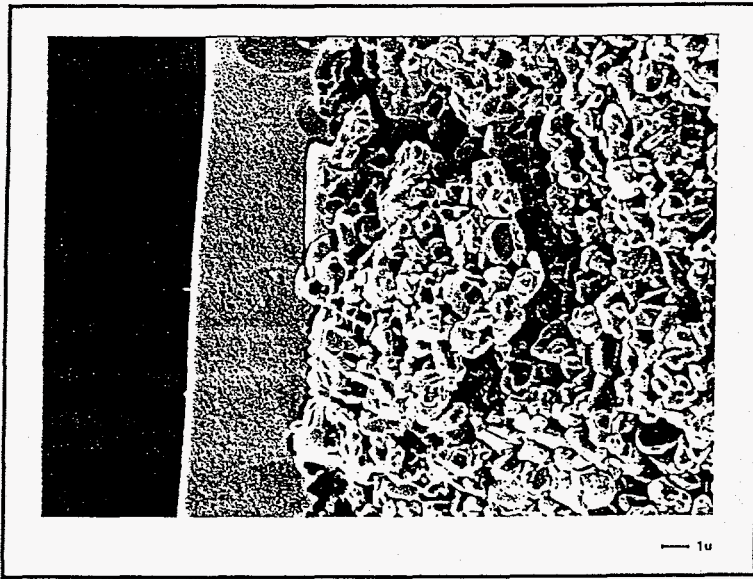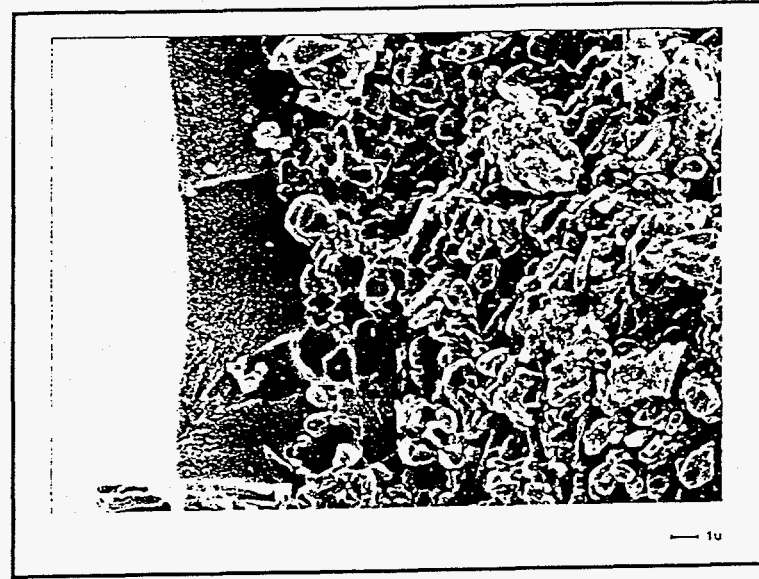
Title Tube 18 bottom MA18B1		Date 04-07-95	Time 10:01
Comment x-section at coating/support interface			
Mag x5,000	kV 5 WD 9mm	Spot 6	Scan P3
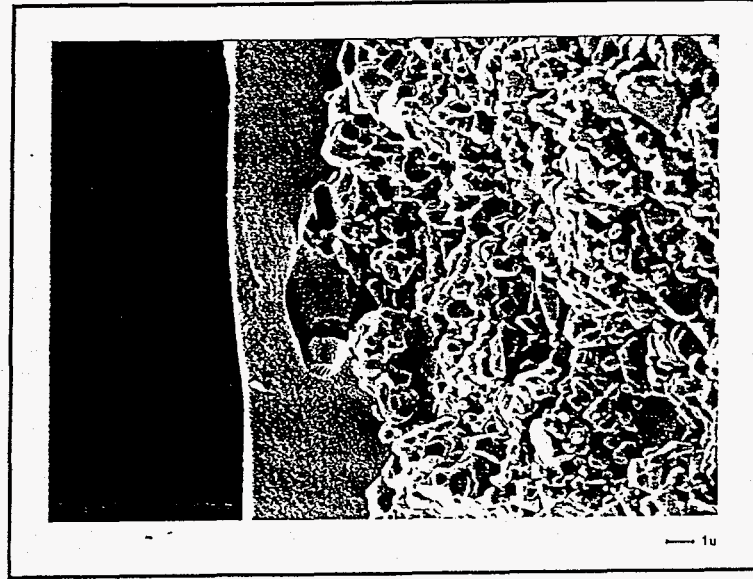
Title Tube 18 bottom MA18B2		Date 04-07-95	Time 10:07
Comment x-section at coating/support interface			
Mag x5,000	kV 5 WD 9mm	Spot 6	Scan P3
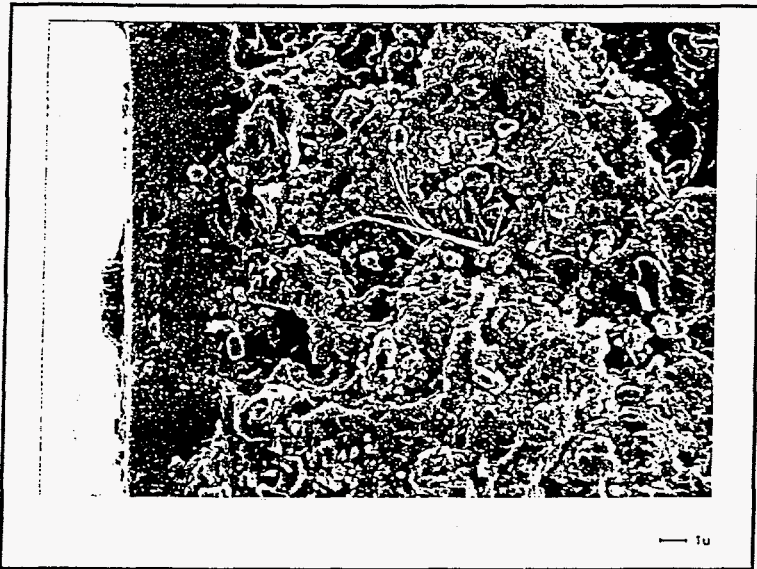
Title Tube 18 bottom 2 MA18B22		Date 04-07-95	Time 10:22
Comment x-section at coating/support interface			
Mag x5,000	kV 5 WD 10mm	Spot 6	Scan P3

Title Tube 18 bottom 2 MA18B21		Date 04-07-95	Time 10:14
Comment x-section at coating/support interface			
Mag x5,000	kV 5 WD 11mm	Spot 6	Scan P3

Figure 13. SEM Showing Coating Uniformity in the Tube Circumference at the Bottom of the Membrane
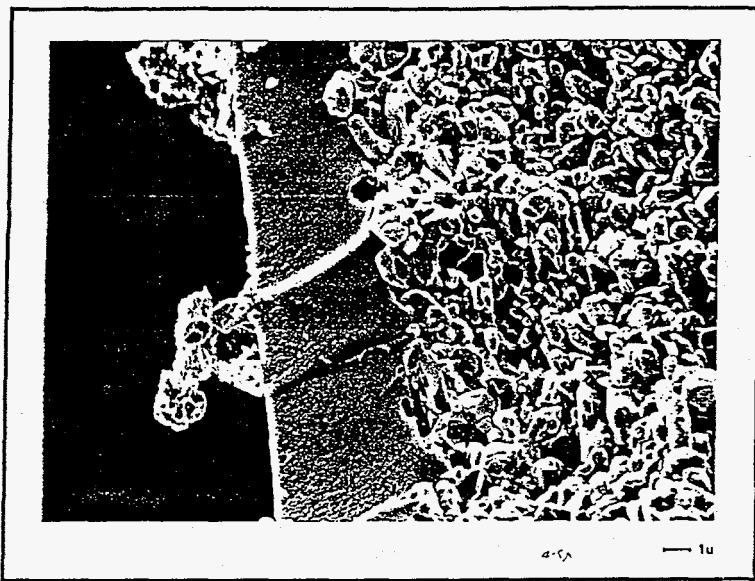
9a
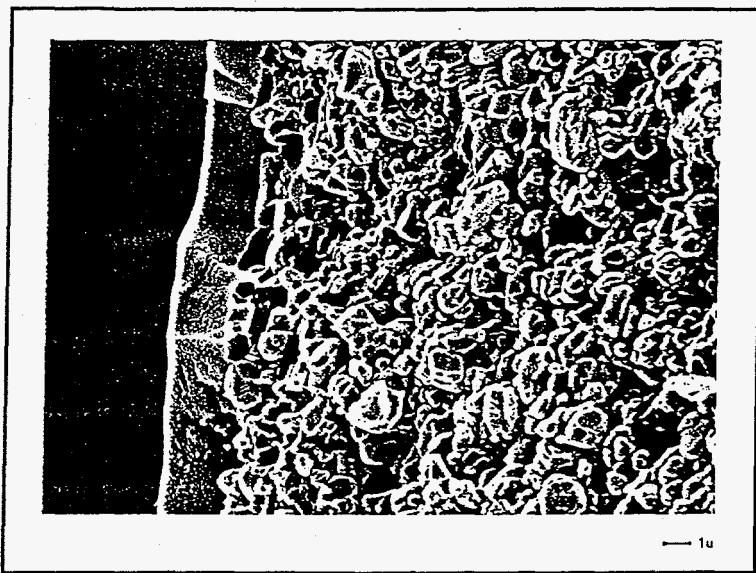
Figure 14. SEM Showing Coating Uniformity in the Tube Circumference at the top of the Membrane

9b

PHASE1.XLS Chart 7

Effect of Passivation on Membrane Performance
FCC mix, 3.0 atm, CH4 sweep

Legend:
- ▲ 0 min
- ● 15 min
- ■ 30 min
- ◆ 60 min
- × 120 min
- ○ 180 min

X-axis: H2 Recovery, %

Y-axis: Propylene rejection, %
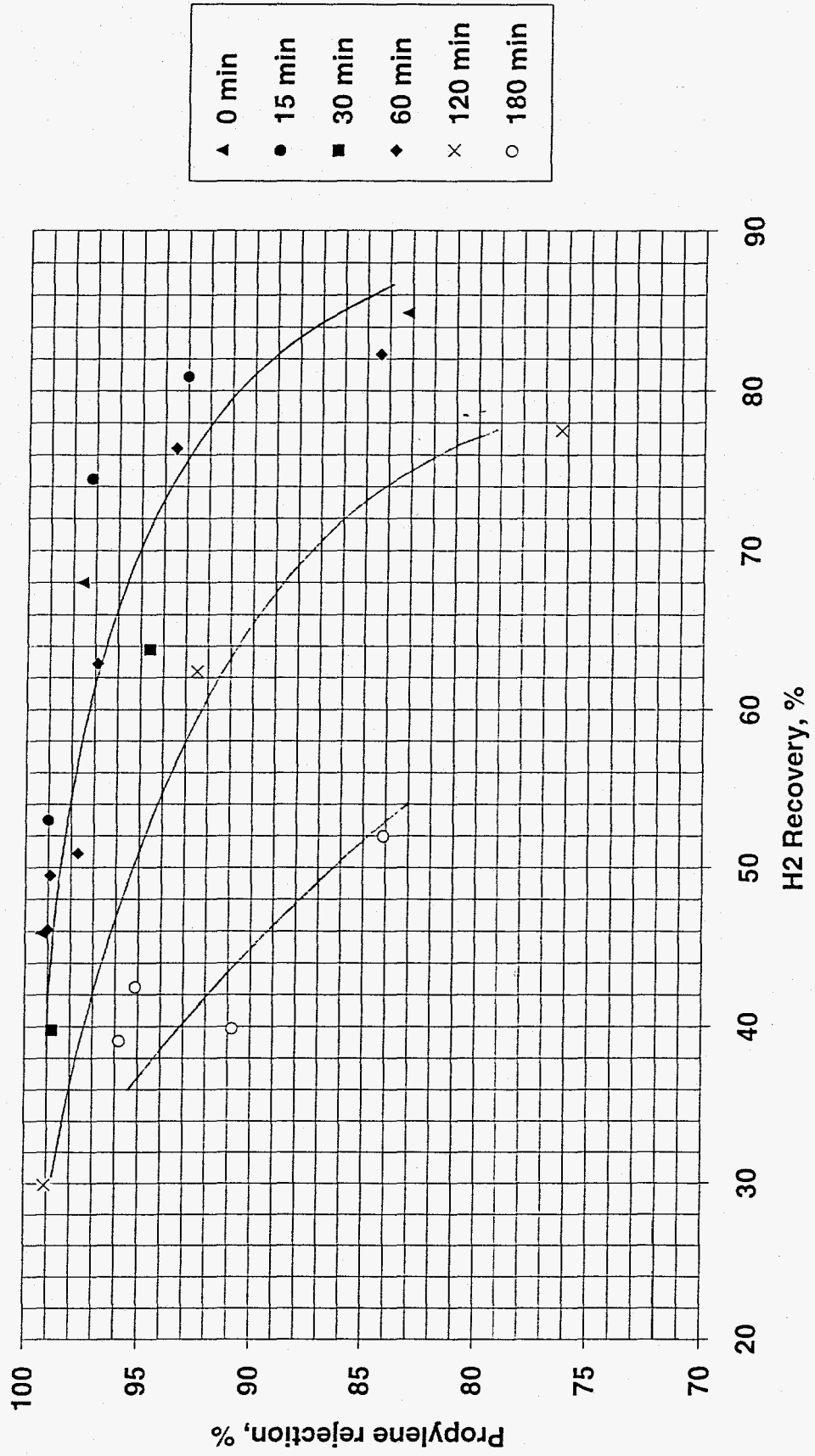
Figure 15. Effect of Passivation Time on Propylene Rejection
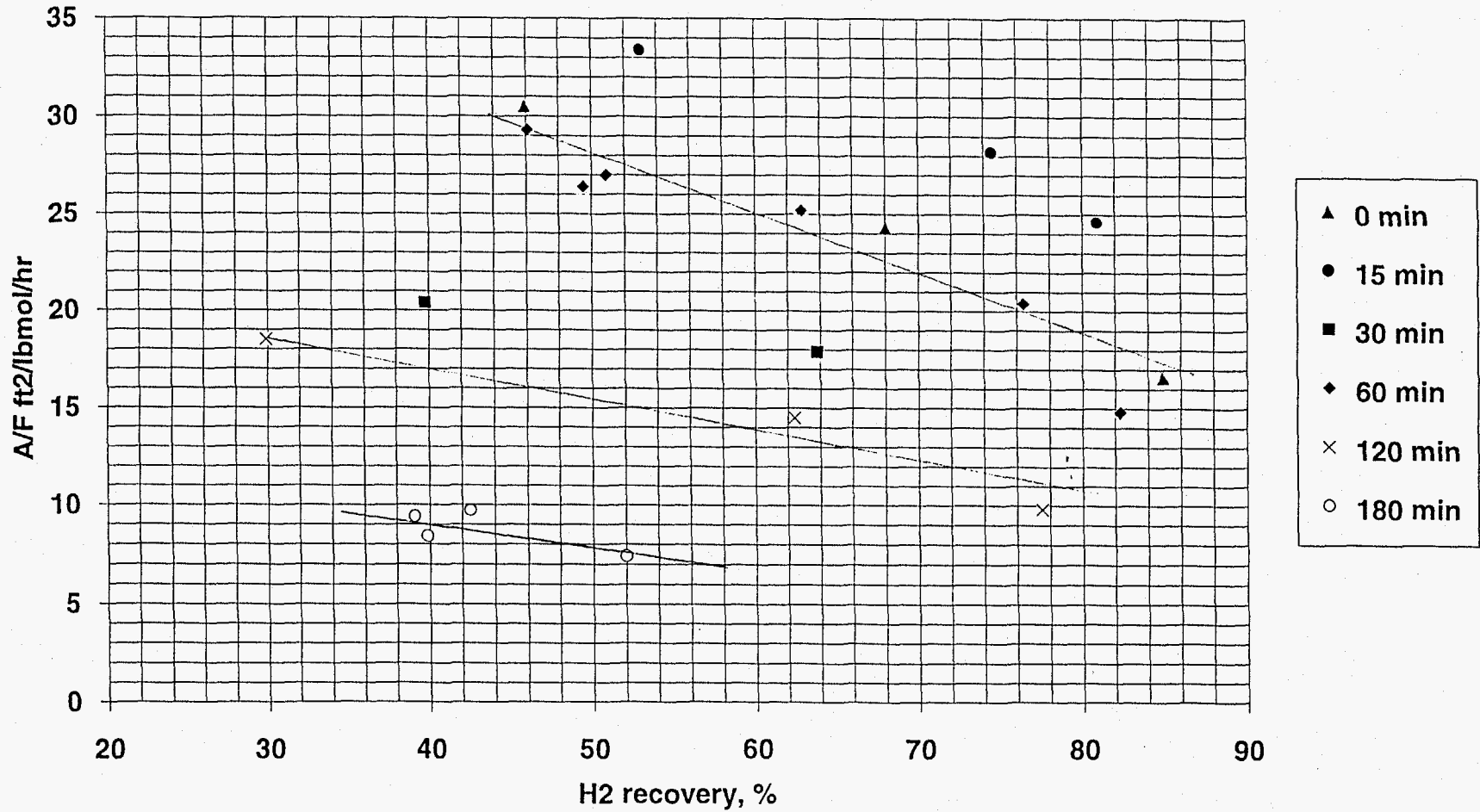
Figure 16. Effect of Passivation Time on Membrane A/F

REPRODUCIBILITY OF SSF MEMBRANE PREPARATION

Tube #	Mass of polymer	He P/l x10E5 B/cm PVDC	Mass of carbon	He P/l x10E5 B/cm membrane	CO2 P/l x10E5 B/cm membrane	H2 recovery membrane	C3= rejection membrane	A/f ft2/lbmol/h membrane
					TABLE 12			
14006-35-1bcl	0.1092	11.0	0.0267	144	331	54	97.6	24.3
14006-35-2bcl	0.1078	10.2	0.0267	116	327	44.8	98.4	27.2
14006-35-3bcl	0.1111	12.4	0.0282	95	337	49.9	97.9	24.4
14006-35-4bcl	0.1089	11.5	0.0269	121	356	51.3	98.4	27.1
14006-35-5bcl	0.1117	15.6	0.0264	135	359	47.6	98.2	24.1
14006-35-6bcl	0.1177	10.7	0.0348	147	402	43.9	97	19.9
14006-35-7bcl	0.1224	14.2	0.0374	190	388	48	96.9	19.9
14006-35-8bcl	0.1189	12.8	0.0371	226	330	48.5	94.8	14.3
14006-35-9bcl	0.1233	11.5	0.0362	165	407	46.4	97.7	19.3
14006-35-10bcl	0.1250	10.8	0.0383	198	349	41.4	91.8	12.9
14006-35-11bcl	0.1156	13.9	0.0336	107	329	55.4	96.6	21.7
14006-35-12bcl	0.1145	12.2	0.0323	155	319	64.6	96.5	22.4
14006-35-13bcl	0.1165	10.8	0.0343	140	393	55.5	96.1	20.2
14006-35-14bcl	0.1221	12.8	0.0345	167	340	50.9	96.4	17.6
14006-35-15bcl	0.1191	10.4	0.0353	160	385	51.7	96.6	20.4
14006-35-16bcl	0.1177	9.7	0.0340	178	379	46.8	97.4	20.6
14006-35-17bcl	0.1210	9.6	0.0362	225	392	44.4	94.3	13.6
14006-35-18bcl	0.1234	20.1	0.0358	278	412	45.5	81.6	7.7
14006-35-19bcl	0.1236	14.1	0.0356	244	398	37.6	95.3	12.7
14006-35-20bcl	0.1225	17.5	0.0341	228	396	52.5	90.2	13.1
14006-35-1	0.1305	23.2	0.0366	167	383	52.2	93.5	20.0
14006-35-2	0.1323	13.8	0.0364	173	374	40.3	95.8	20.1
14006-35-3	0.1244	12.5	0.0443	173	382	64	96.5	23.6
14006-35-4	0.1347	8.8	0.0329	97	323	61.7	98.3	27.3
14006-35-5	0.1269	19.2	0.0340	184	378	50.6	97.9	24.0
14006-35-6	0.1297	9.7	0.0358	171	399	65.6	95.1	21.1
14006-35-7	0.1216	10.4	0.0300	155	362	64.1	97.6	27.3
14006-35-8	0.1276	12.3	0.0334	185	401	38.6	99.1	24.0
14006-35-9	0.1244	12.2	0.0340	202	427	55.2	95.8	19.4
14006-35-10	0.1193	8.8	0.0325	179	367	47.4	98.8	27.7
14006-35-11	0.1229	12.3	0.0332	165	365	33.9	99	21.6
14006-35-12	0.1223	9.3	0.0304	163	384	80.7	93.5	21.5
14006-35-13	0.1250	12.5	0.0445	175	379	47.2	98.5	24.2
14006-35-14	0.1226	12.6	0.0320	161	378	63.1	96.8	24.5
14006-35-15	0.1257	17.7	0.0327	172	405	52.3	97.6	21.6
14006-35-16	0.1289	11.7	0.0323	200	423	32.8	98.6	21.3
14006-35-17	0.1243	10.4	0.0326	179	335	50.5	97.2	21.4
14006-35-18	0.1107	9.9	0.0283	174	312	80.7	92.7	21.4
14006-35-19	0.1342	16.7	0.0349	179	350	34.6	98.3	19.1
14006-35-20	0.1198	9.9	0.0319	110	331	45.1	98.7	38.0
bcl tubes								
Average	0.1176	12.6	0.0332	171	366.5			
Std dev.	5.50E-03	2.70E+00	4.00E-03	49.5	31.6			
others								
Average	0.1254	12.7	0.0341	168.1	372.9			
Std dev.	5.60E-03	3.80E+00	4.10E-03	25	31.2			

REPRODUCIBILITY OF SSF MEMBRANE PREPARATION

					TABLE 13			
Tube #	Mass of polymer	He P/l x10E5 B/cm PVDC	Mass of carbon	He P/l x10E5 B/cm membrane	CO2 P/l x10E5 B/cm membrane	H2 recovery membrane	C3= rejection membrane	A/f ft2/lbmol/h membrane
14006-20-1	0.1199	8.1	0.0308	65.2	294	56.3	96.9	33.5
14006-20-2	0.1278	6.9	0.0337	94.1	395	50.9	97.9	26.7
14006-20-3	0.1143	4.6	0.0299	78	298	53.9	97.6	34.2
14006-20-4	0.1166	6	0.0311	93	423	47.8	98.2	28.4
14006-20-5	0.12	8.7	0.0324	101.3	435	39.8	98.5	24.5
14006-20-6	0.1186	8.8	0.0319	105.4	475	46.3	98.2	22.4
14006-20-7	0.1325	6.5	0.0361	59.5	262	51.5	97.6	37.9
14006-20-8	0.1342	8.2	0.0344	80.8	415	50.7	97.7	27.3
14006-20-9	0.1357	7.5	0.031	101.5	429	47.1	98.2	25.1
14006-20-10	0.1247	8.8	0.0331	101.1	471	46.8	98.8	26.5
14006-20-11	0.1267	9.8	0.0351	94.6	408	44.4	98.5	25.3
14006-20-12	0.1249	8.9	0.0321	118	390	30.5	96.6	16.9
14006-20-13	0.1179	9.5	0.0305	108	400	39	97.6	19.3
14006-20-14	0.1172	8.7	0.0291	102	411	47.6	98.3	23.7
14006-20-15	0.1138	9.9	0.0293	106.3	407	44.9	97	20.9
14006-20-16	0.1305	8.1	0.0279	118.3	446	37.2	96.6	17.3
14006-20-17	0.121	13.7	0.0289	96.9	398	42.9	98.3	24.7
14006-20-18	0.1293	10.2	0.0306	101.8	438	34.2	98.8	25.3
14006-20-19	0.1377	11.9	0.0341	70.4	340	48.2	98.4	35
14006-20-20	0.1353	11	0.0347	81.4	367	46.4	98.1	27.5
14006-20-21	0.112	8.9	0.0281	129.1	432	38.6	98.3	22.9
14006-20-22	0.1174	8.1	0.0346	90.9	362	40.1	97.2	24.8
14006-20-23	0.1846	9.3	0.0387	84.9	425	44.7	98.6	27.7
14006-20-24	0.1441	14.7	0.0548	100.8	425	39.8	98.6	23
14006-20-25	0.1275	13.4	0.0318	95.2	449	55.6	97.5	23.3
Average	0.1275	9.2	0.0354	95.1	400			
Std dev.	1.46E-02	2.35E+00	1.41E-02	16.4	53.6			

of CO_2 is greater than that of helium. This screening test is not successful in distinguishing between marginal, good or very good tubes. Thus, the value of this test is strictly in screening to determine if mixed gas permeation tests should be carried out.

3.5 Mixed Gas Performance Characteristics

Mixed gas performance properties of the SSF membranes were measured using a hydrogen/hydrocarbon mixture. This gas mixture, referred to as the refinery Fluid Catalytic Cracker (FCC) off-gas, contains 20% H_2, 20% CH_4, 8%C_2H_4, 8%C_2H_6, 15% C_3H_8,and 29% C_3H_6. The performance definitions with pure and mixed gases were shown in **Table 1**. For the SSF membrane, the objective is to simultaneously maximize the H_2 recovery in the high pressure effluent and the rejection of the other components, viz. hydrocarbons, to the permeate side so that the H_2-enriched stream is recovered as the high pressure effluent. In addition to the rejections of hydrocarbons at different hydrogen recoveries, the membrane area required for the separation is an important membrane performance characteristic. This is noted as A/F where A is the membrane geometric area and F the feed rate to the membrane at the specific hydrogen recovery.

Figures 17-22 show some typical mixed gas membrane performance characteristics with the SSF tubular membranes using the FCC gas at a feed pressure of 3 atm and sweeping with methane at ~1atm. The data show the following :
(i) As the hydrogen recovery in the high pressure effluent increases, the hydrocarbon rejection to the permeate stream decreases.
(iii) The highest rejection from the mix is the species most selectively adsorbed (propylene) and the rejection decreases for the less selectively adsorbed species ($C_3>C_2>C_1$).
(iii) For example, at 50% hydrogen recovery, the propylene and propane rejections are >98% and >97%, respectively.
(iv) The membrane area increases at lower hydrogen recoveries (i.e., higher hydrocarbon rejections). This indicates that the membrane area required for separation is higher if more hydrocarbon molecules permeate to the low pressure side of the membrane.
(v) There can be a significant variability in the membrane A/F from tube to tube, perhaps due to small differences in the support or membrane structure **(Figure 22)**.

The membranes were also tested at feed pressures of 5 atm. The data show that the membrane separation properties are not changed with this gas mixture except that the A/F expectedly decreases as the feed pressure is increased **(Figure 22)**.

With the above benchmark data from some tubes, an effort was initiated to prepare a larger number of tubes which would demonstrate reproducibilty and lot-to-lot variability in membrane performance. In addition, these tubes would be used in a multi-tube module so that a larger membrane area could be tested in addition to developing the module design and scale-up criteria.

H2 Recovery vs Propylene Rejection, FCC gas, 3.0 atm, CH4 sweep,
S/F=0.15
Tubes

Propylene rejection, %
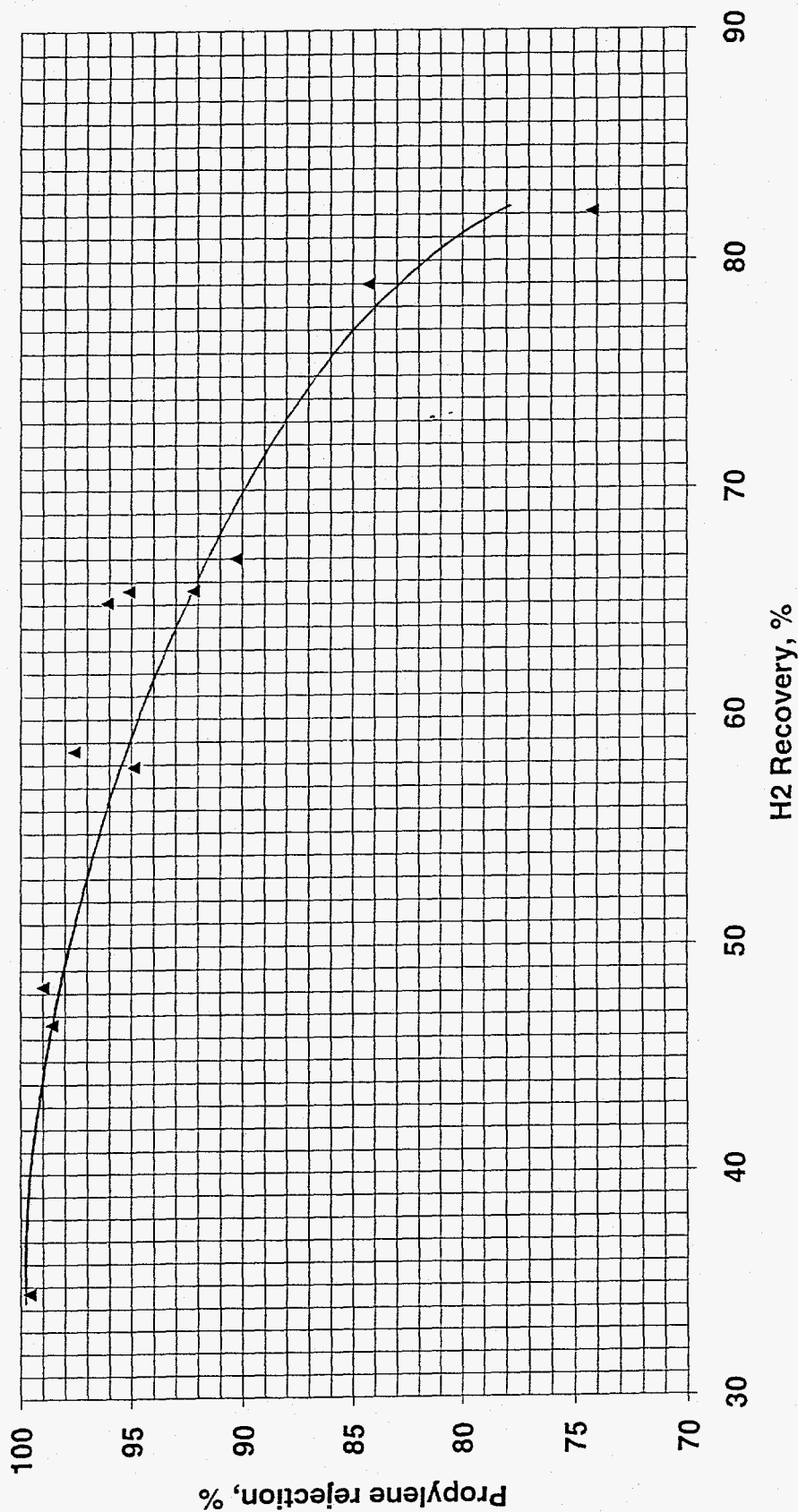
H2 Recovery, %

Figure 17. Typical H$_2$ Recovery vs Propylene Rejection Profiles for Tubes
Coated with SSF Membrane and Tested with FCC Mix

10a

H2 Recovery vs Propane Rejection, FCC gas, 3.0 atm, CH4 sweep, S/F=0.15
Tubes

Figure 18. Typical H$_2$ Recovery vs Propane Rejection Profiles for Tubes
Coated with SSF Membrane and Tested with FCC Mix

1oc

PHASE1.XLS Chart 3

H2 Recovery vs Ethylene Rejection, FCC gas, 3.0 atm, CH4 sweep, S/F=0.15
Tubes

Ethylene Rejection, %
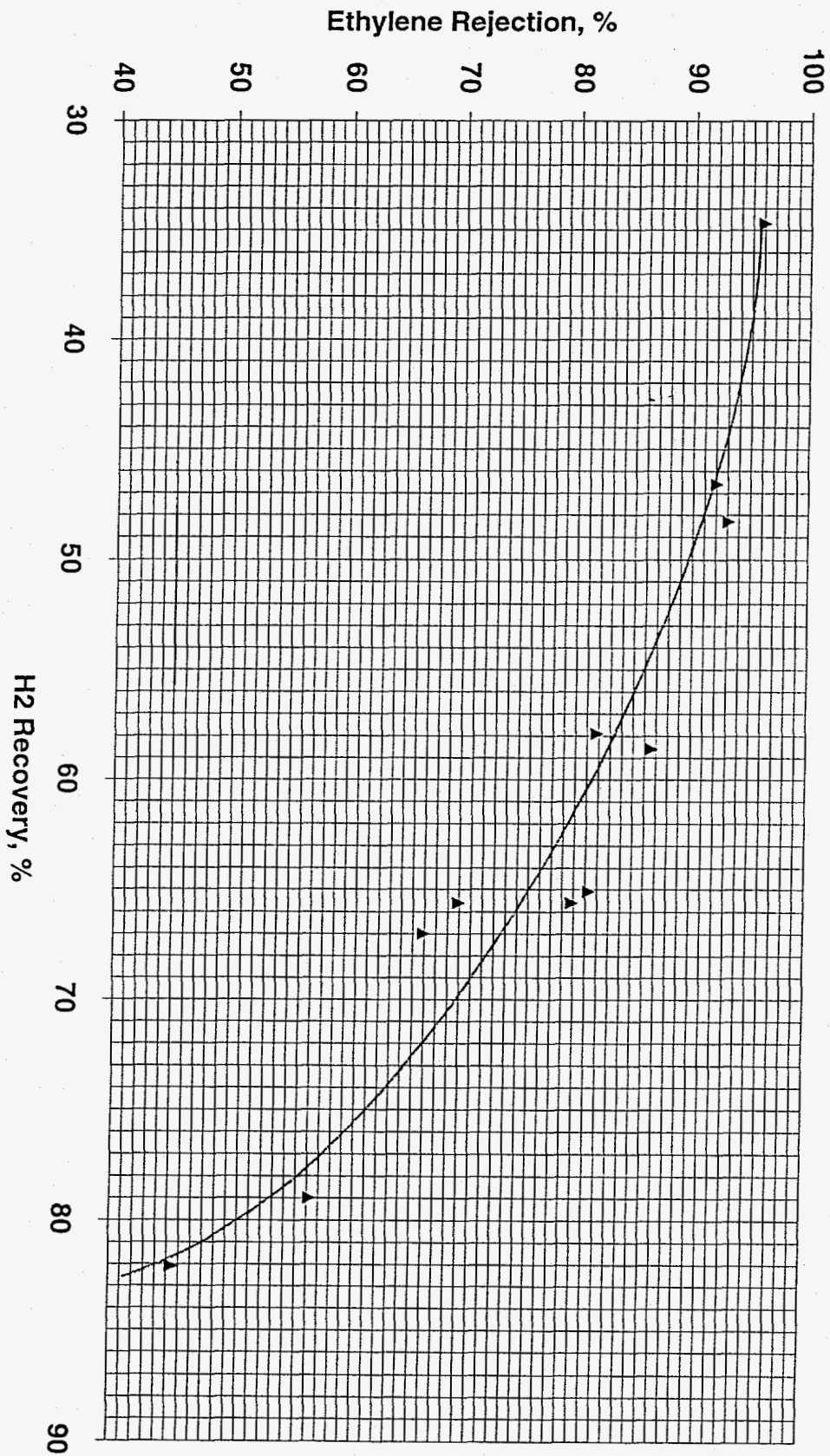
H2 Recovery, %

Figure 19. Typical H2 Recovery vs Ethylene Rejection Profiles for Tubes
Coated with SSF Membrane and Tested with FCC Mix.

H2 Recovery vs Ethane Rejection, FCC gas, 3.0 atm, CH4 sweep, S/F=0.15
Tubes
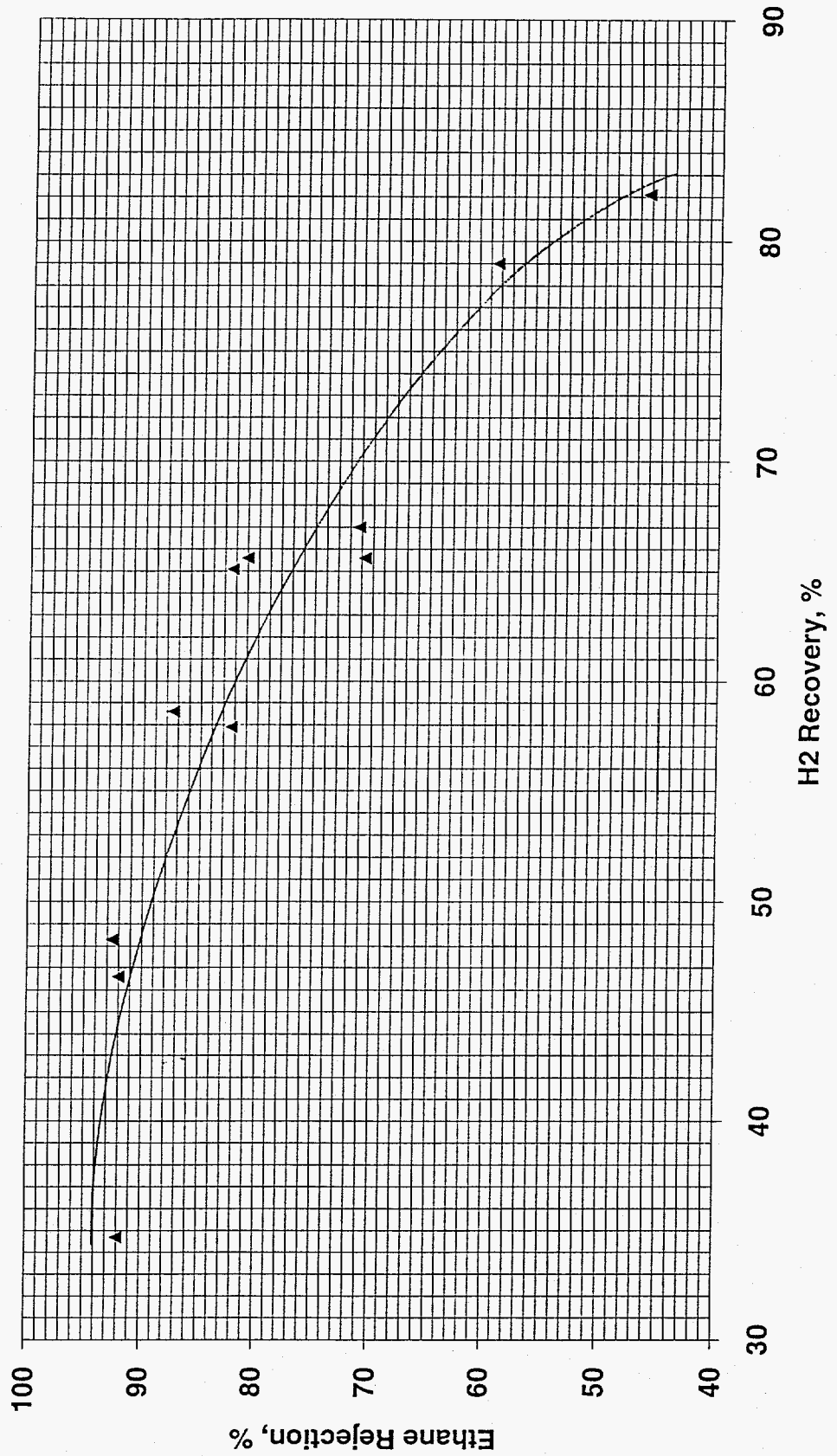
Figure 20. Typical H_2 Recovery vs Ethane Rejection Profiles for Tubes
Coated with SSF Membrane and Tested with FCC Mix.

H2 Recovery vs Methane Rejection, FCC gas, 3.0 atm, CH4 sweep, S/F=0.15 Tubes
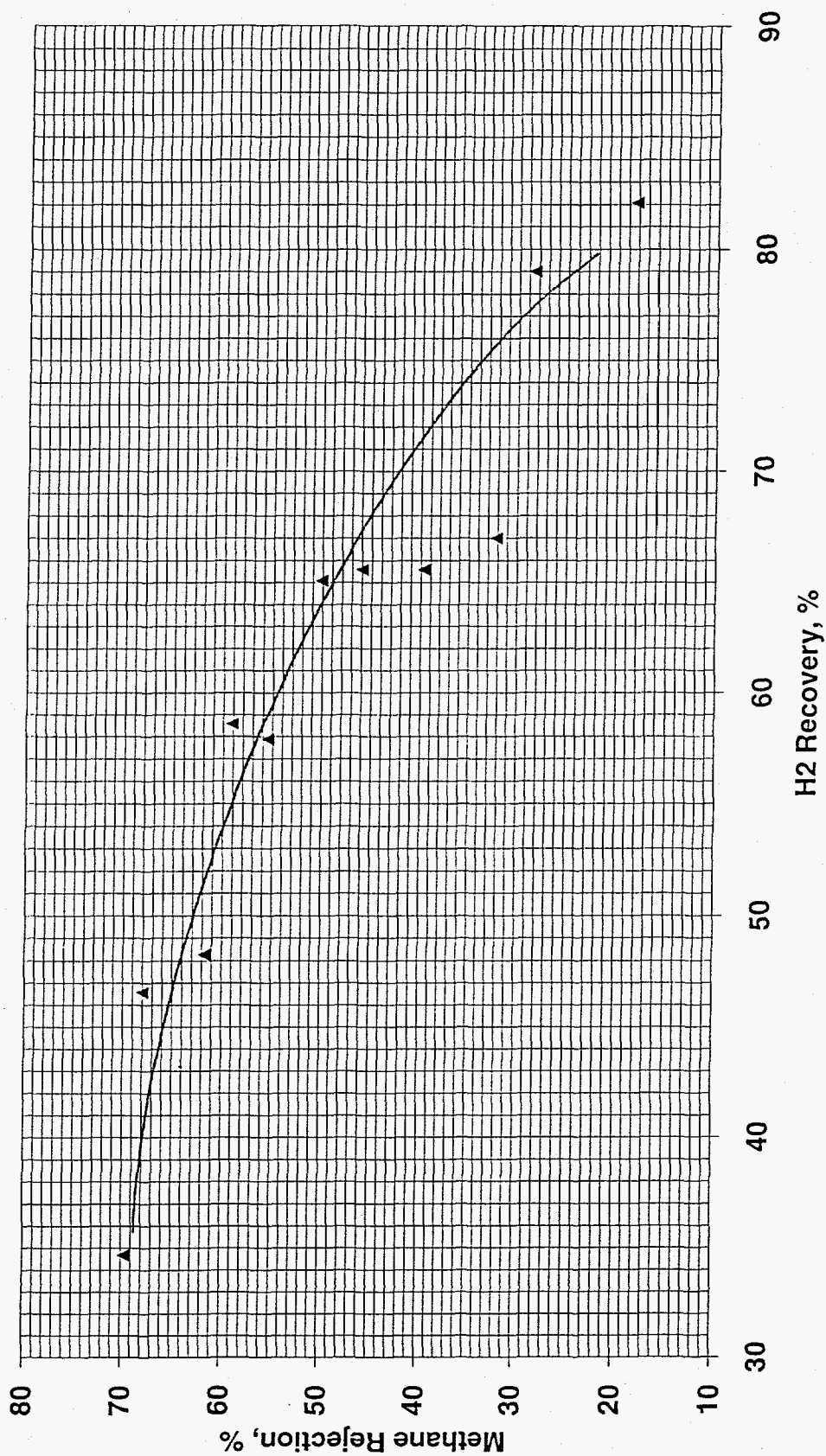
Figure 21. Typical H$_2$ Recovery vs Methane Rejection Profiles for Tubes Coated with SSF Membrane and Tested with FCC Mix

PHASE1.XLS Chart 6

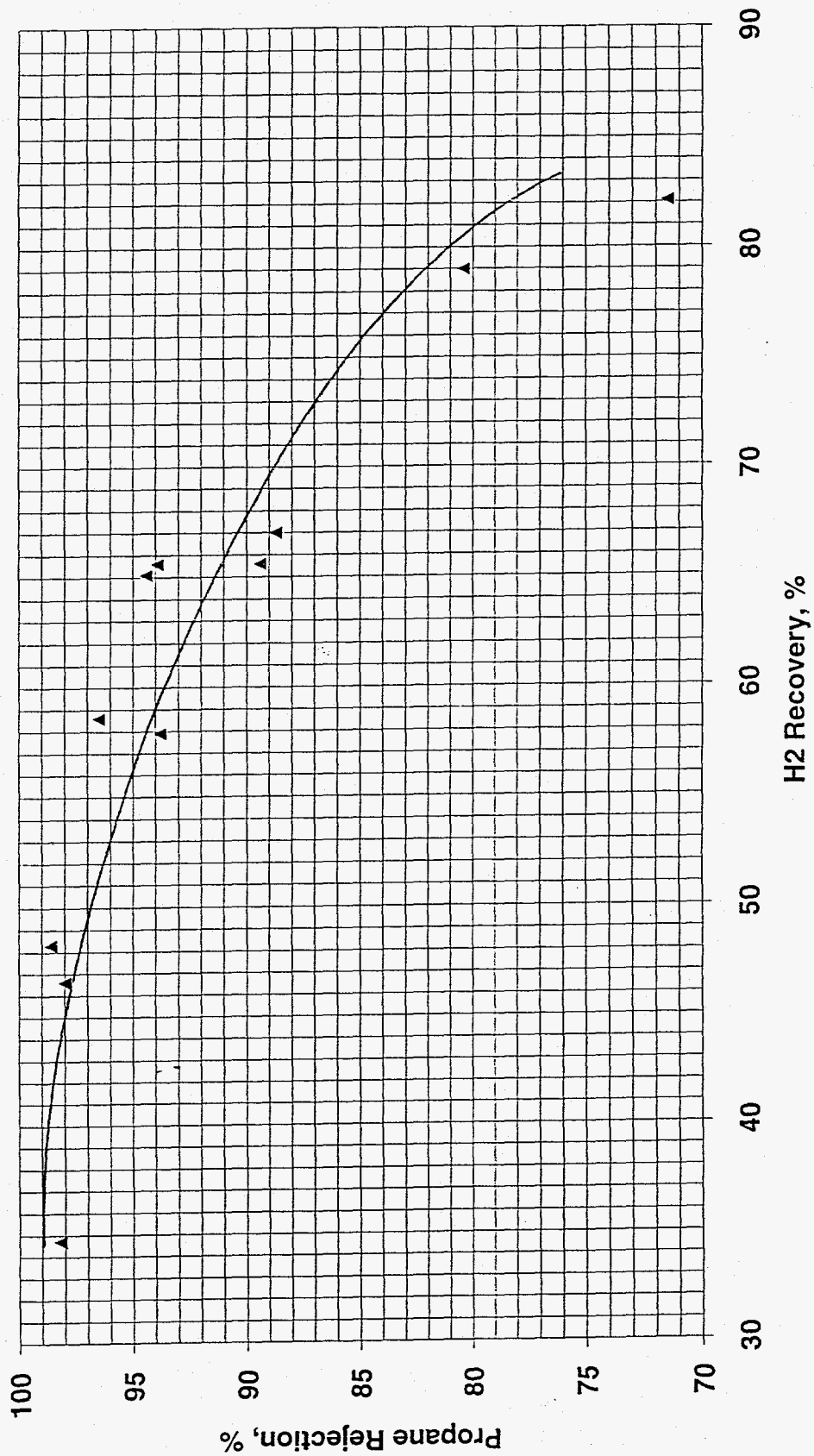H2 Recovery vs A/F, FCC gas, 3.0 atm, CH4 sweep, S/F=0.15
Tubes
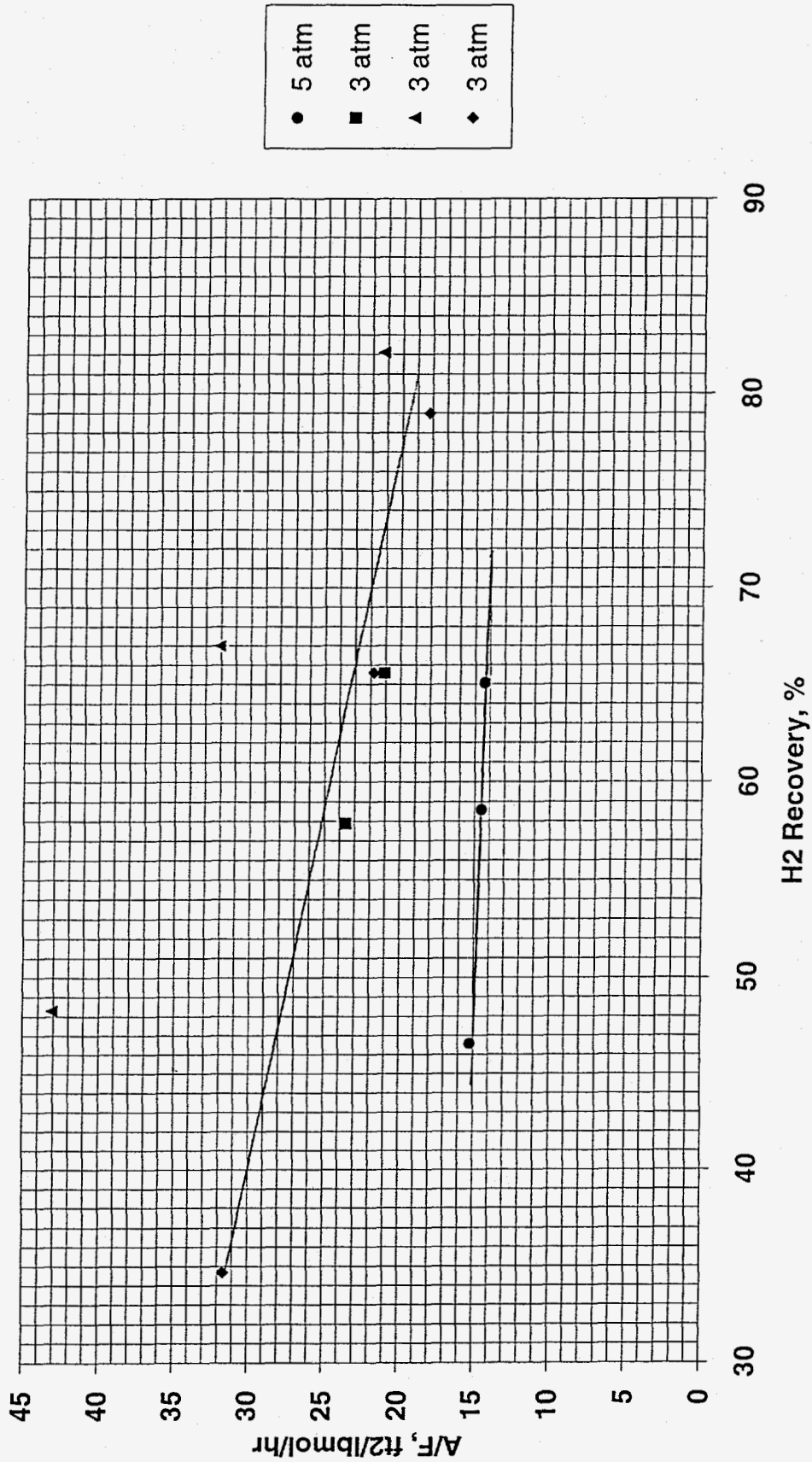
Figure 22. Typical H$_2$ Recovery vs Membrane A/F Profiles for Tubes
Coated with SSF Membrane and Tested with FCC mix; note
lower A/F at higher pressures

3.6 Design/Construction of Multi-Tube Module

One of the deliverables in this program is the scale-up of the SSF membrane from single tubes to multiple tubes in a housing. A module was designed to house 19 tubes which represent 1 ft^2 of membrane area. A triangular pitch hexagonal shaped layout with a center-to-center distance of 1.3 x Tube O.D was designed and built. The details of the module are shown in **Figure 23**.

The module has the capability of being fed from the top or the bottom and with a countercurrent or co-current sweep. The module was cleaned with a hydrocarbon solvent followed by a low boiling point halogenated solvent to remove contamination after welding.

3.7 Design/Construction of Membrane Module Test Unit

A membrane test unit was designed to test the performance of the 1 ft^2 membrane area module. The key features of this system are :

(i)   Gas supply through individual cylinders so that suitable gas mixtures can be blended. Single gas tests can also be performed.
(ii) On-line gas chromatograph (GC) for analysis of feed, effluent and permeate streams.
(iii) Variable pressure (max 125 psig) and flow rate (max 50 liters/min) capability so as to be able to deliver different gas flow rates at a fixed pressure.
(iv) Capability of feeding gas to membranes from 0.2 to 2 ft^2 in membrane area.
(v)   Safety alarms, shrouds and shutdown for flammable gas handling.

The process and instrumentation diagram (PID) for the system is shown in **Figure 24**. The system was constructed, debugged and put into operation. A photogarph of the system is shown in **Figure 25**.

3.8 Fabrication of Tubes for Multi-Tube Module

Tubes were coated with the SSF membrane as described in section 3.3. Each tube was tested with pure and mixed gases. Some of the membrane characteristics from these runs were summarized in **Tables 12 and 13**. Some results from mixed gas testing are shown in **Figures 26-27**. The data for these two sets show that :

(i) About 85% of the tubes prepared meet the recovery-rejection criteria as shown by the dashed line in **Figure 26**.

(ii) There is some variability in the tube A/Fs; some of the tubes have a high A/F and hence may not meet the overall membrane performance criteria of acceptable separation and permeability properties. The reasons for these variations are not clear, but could be related to small changes in the membrane or support pore size from tube to tube.
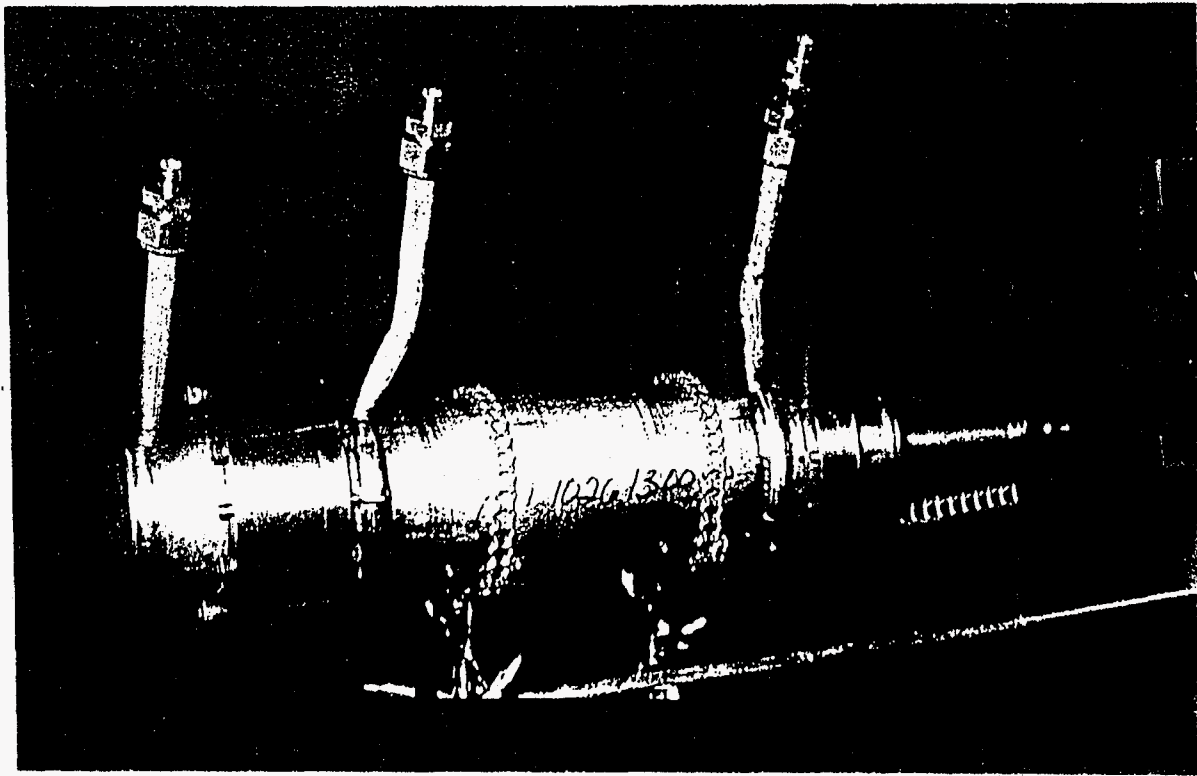
(a)
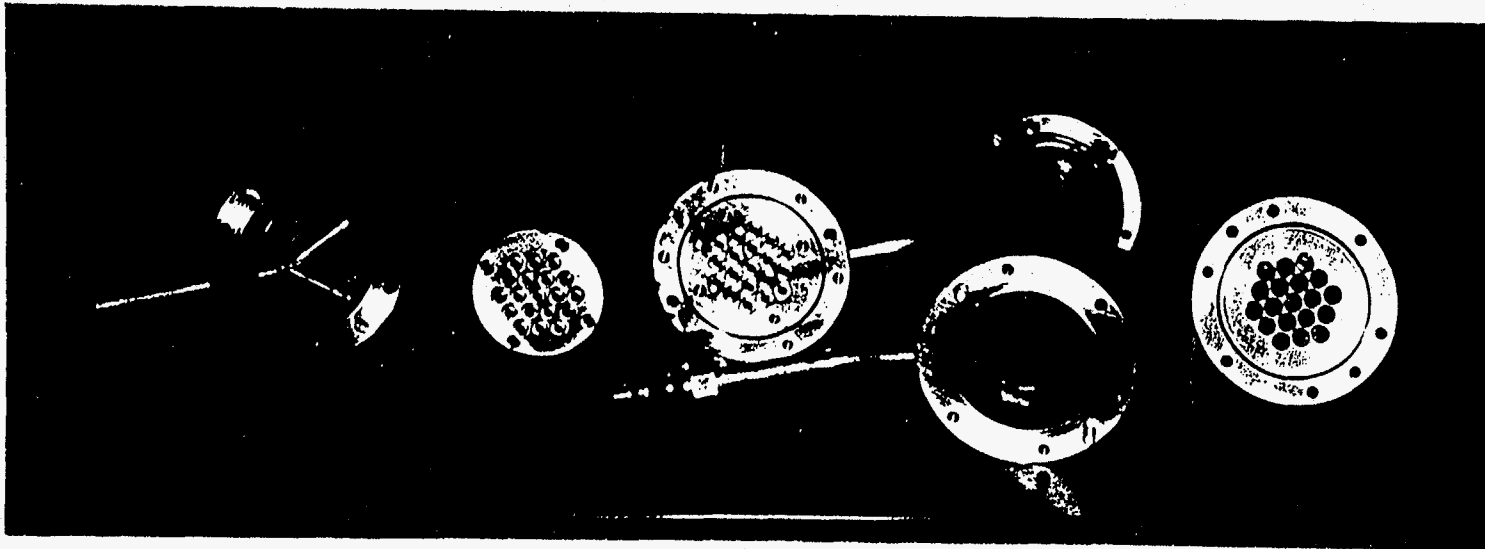
(b)

Figure 23. Multi-Tube Module Shell (a) and Interior Parts (b)
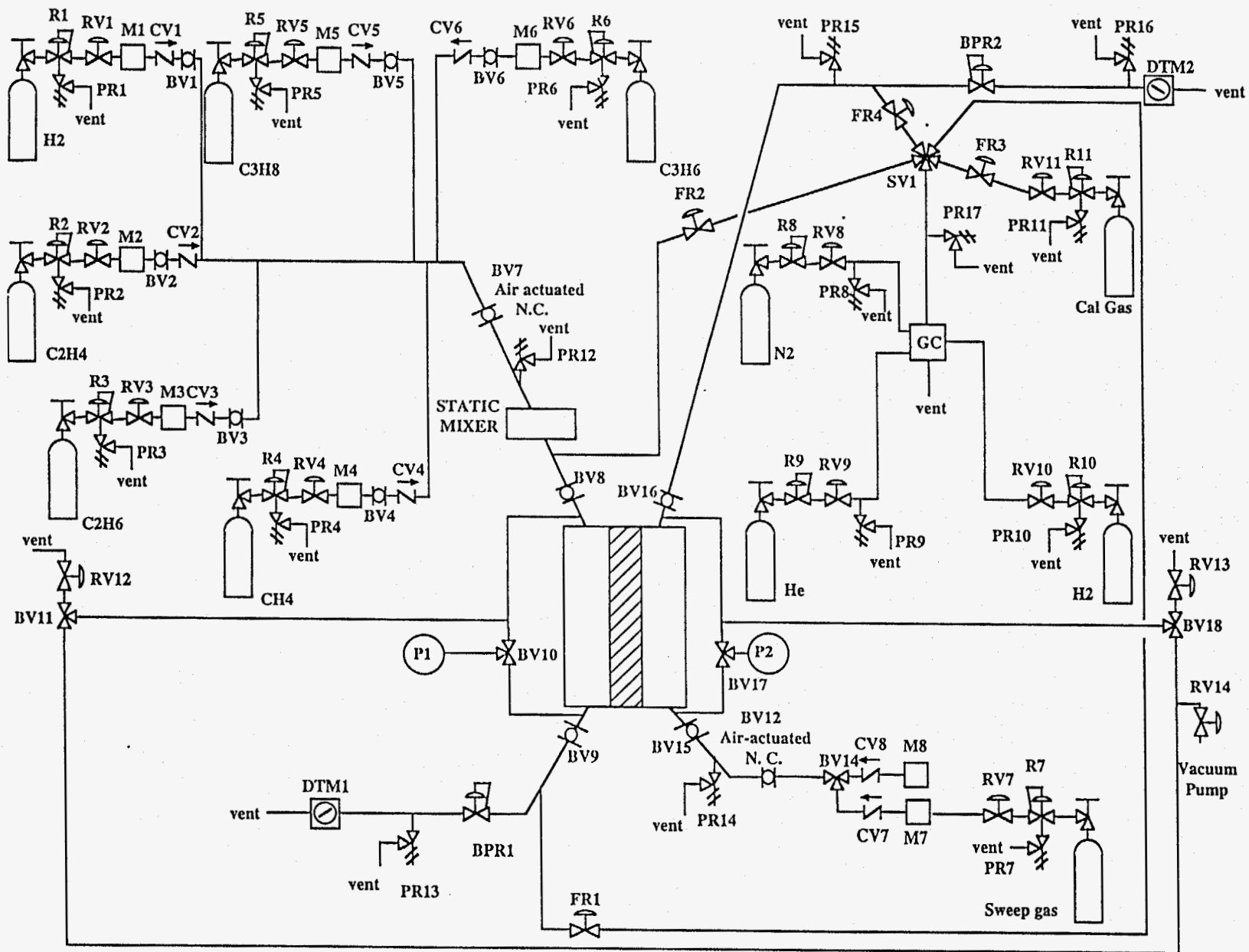
Figure 24. PID for Membrane Test Apparatus

Figure 25. Photograph of Membrane Test Apparatus
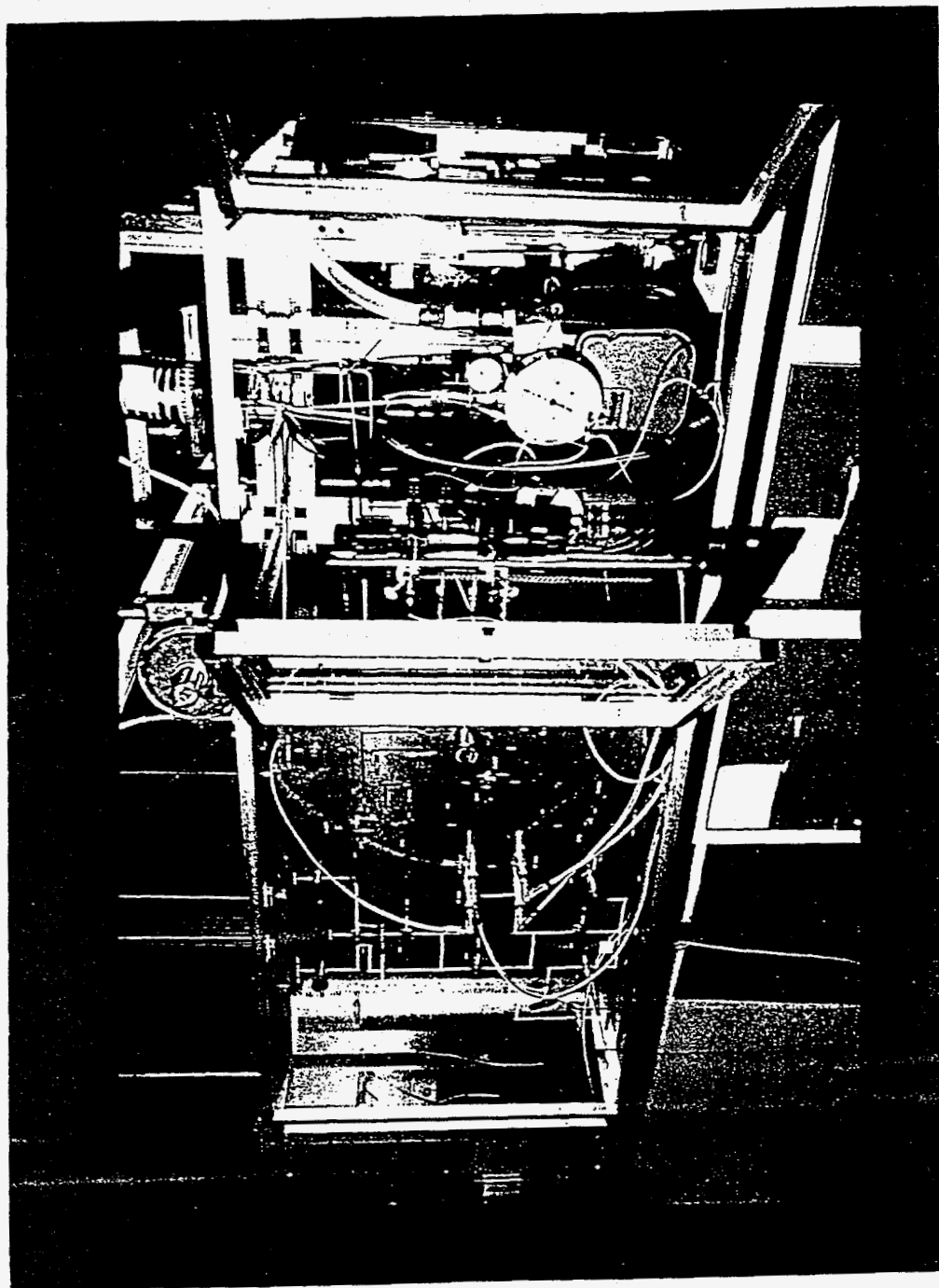
Performance of SSF Tubes with FCC Mix
Data from 60 Tubes
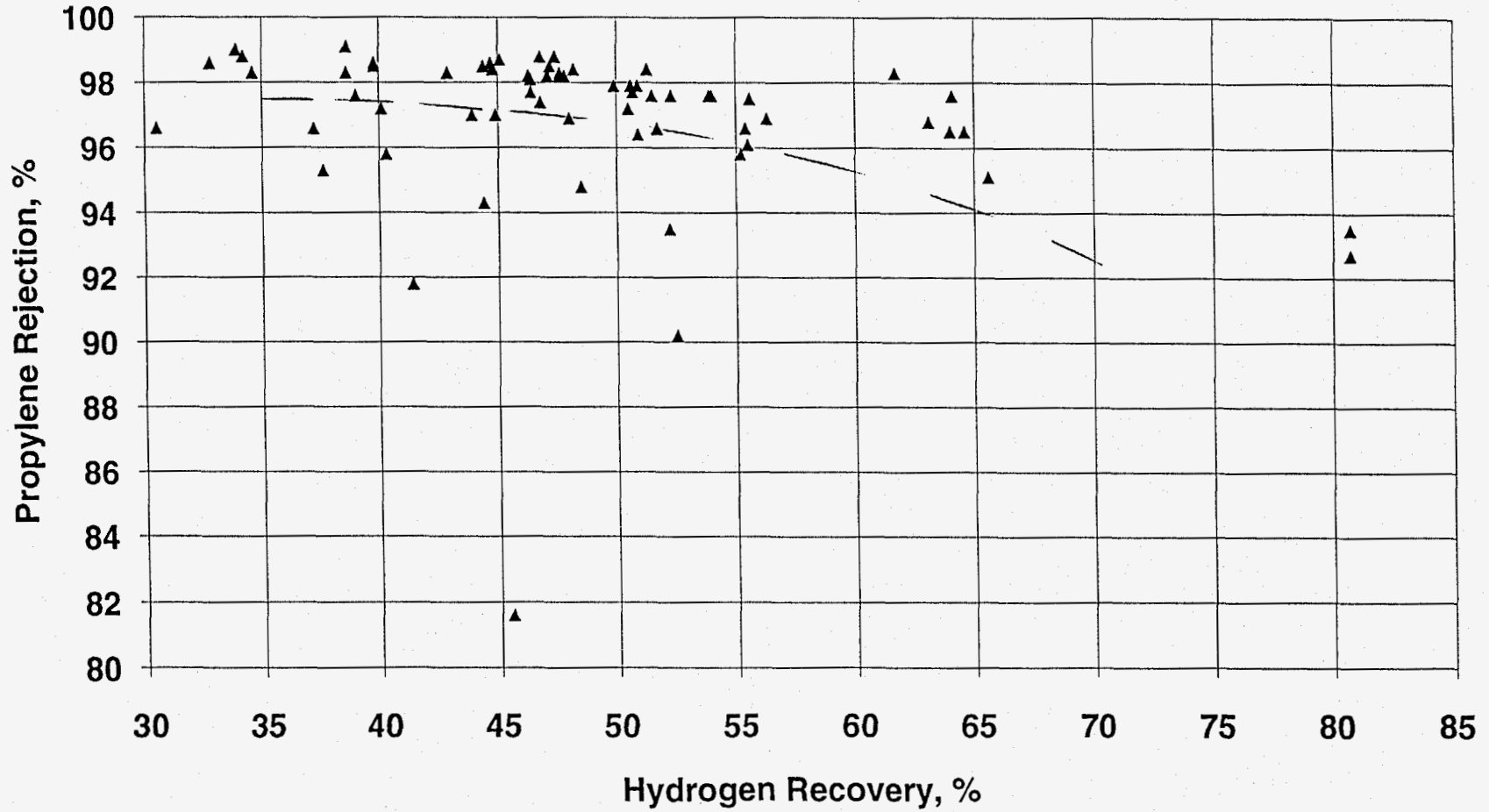
Figure 26. Performance Data from 60 Tubes : H_2 Recovery vs
Propylene Rejection

Performance of SSF Membranes with FCC Mix Data from 60 Tubes
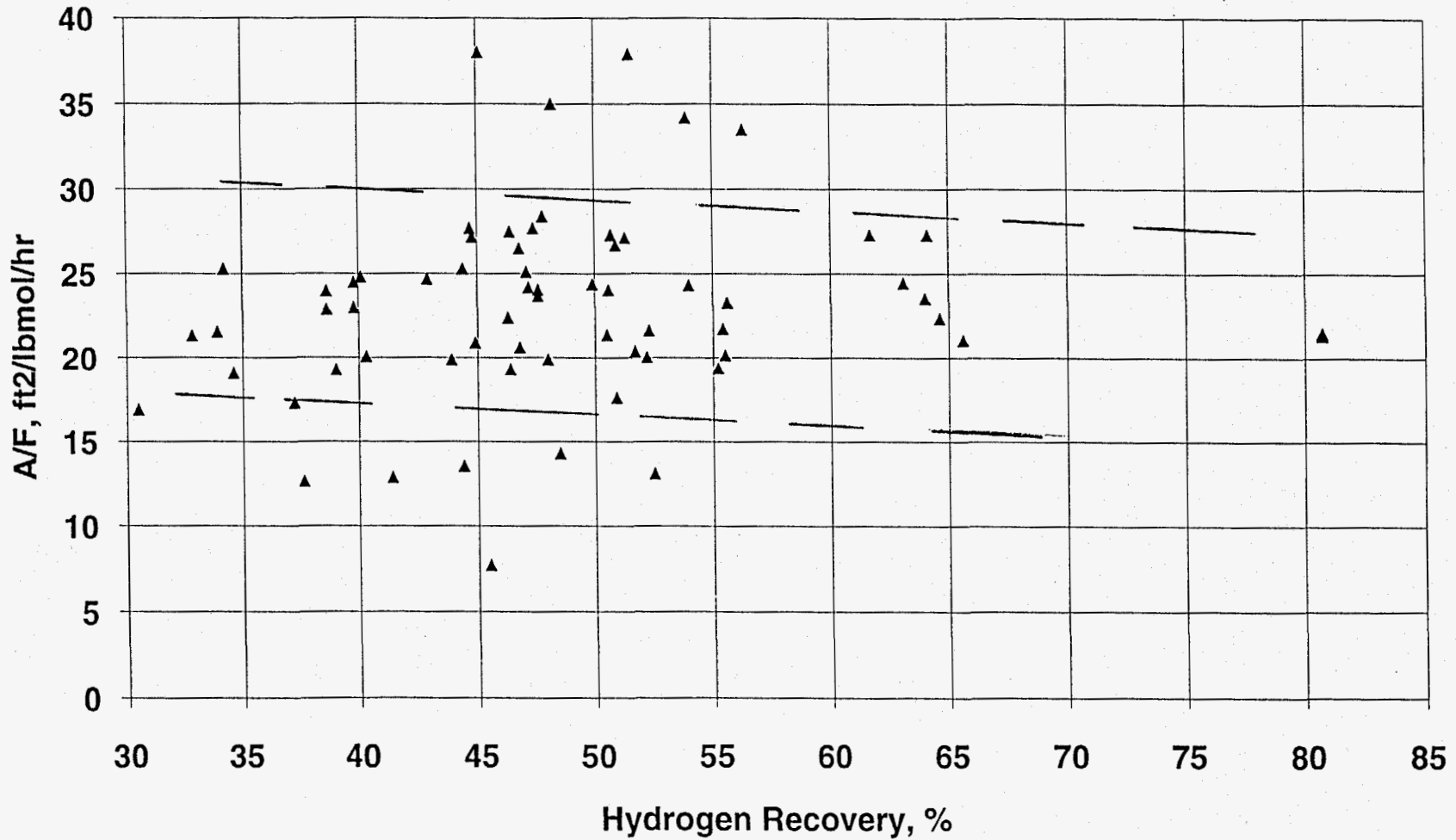
Figure 27. Performance Data from 60 Tubes : H_2 Recovery vs A/F

These tubes were used in the 19-tube module.

3.9 Performance of Multi-Tube Module

3.9.1 Multi-Tube Baseline Data

Nineteen of the above tubes that met the separation criteria and were in the A/F range of 20-28 ft^2/lbmol/hr were selected and assembled in the multi-tube module. Each tube was sealed in the module and the module was checked for external leaks and tested with pure He and CO_2 to ensure that there were no internal leaks. The He and CO_2 permeances were close to those for the individual tubes.

The multi-tube module was tested with the FCC gas mix at 3.0 and 7.0 atm feed pressures and a permeate pressure of ~1.05 atm. The membrane was fed from the bottom and the sweep was countercurrent, with the permeate collected at the bottom and the non-permeate stream collected at the top of the module. The membrane performance data is shown in **Figures 28-35**. Along with the multi-tube module data is the data for the individual tubes assembled in the bundle. The data show the following :

(i) The separation property of the bundle is an average of the individual tubes, with the overall performance at target separation for all the gas components.

(ii) The A/F for the multi-tube module is higher by 20-30% vs individual tubes. The reasons for this are not clear but may be related to either incomplete utilization of the membrane tube area (the sweep gas is introduced a few cm below the top end of the tube) or due to gas maldistribution in the module.

(iii) With the FCC mix, the membrane separation performance is not changed significantly at the higher feed pressure (note that the ethane and ethylene rejections are lower and CH_4 rejection is higher at 7.0 atm vs at 3.0 atm). The overall H_2 purity in the high pressure effluent stream is unaffected.

(iv) The membrane A/F decreases from ~30 ft^2/lbmol/hr at 3.0 atm to ~10ft^2/lbmol/hr at 7.0 atm, thus profoundly reducing the membrane area required to handle a fixed feed flow rate at the higher feed pressure.

3.9.2 Stability of SSF Membrane

The SSF membrane was continuously tested for a 2-month period and the recovery-reject data generated over this period. The feed gas was pretreated to remove moisture and C_5+ hydrocarbons. These data are also included in **Figures 28-35**. The relatively tight scatter in the data indicates that membrane performance did not deteriorate during this test period and that the membrane is stable.

FCC Offgas: C3H6 Rejection vs. H2 Recovery
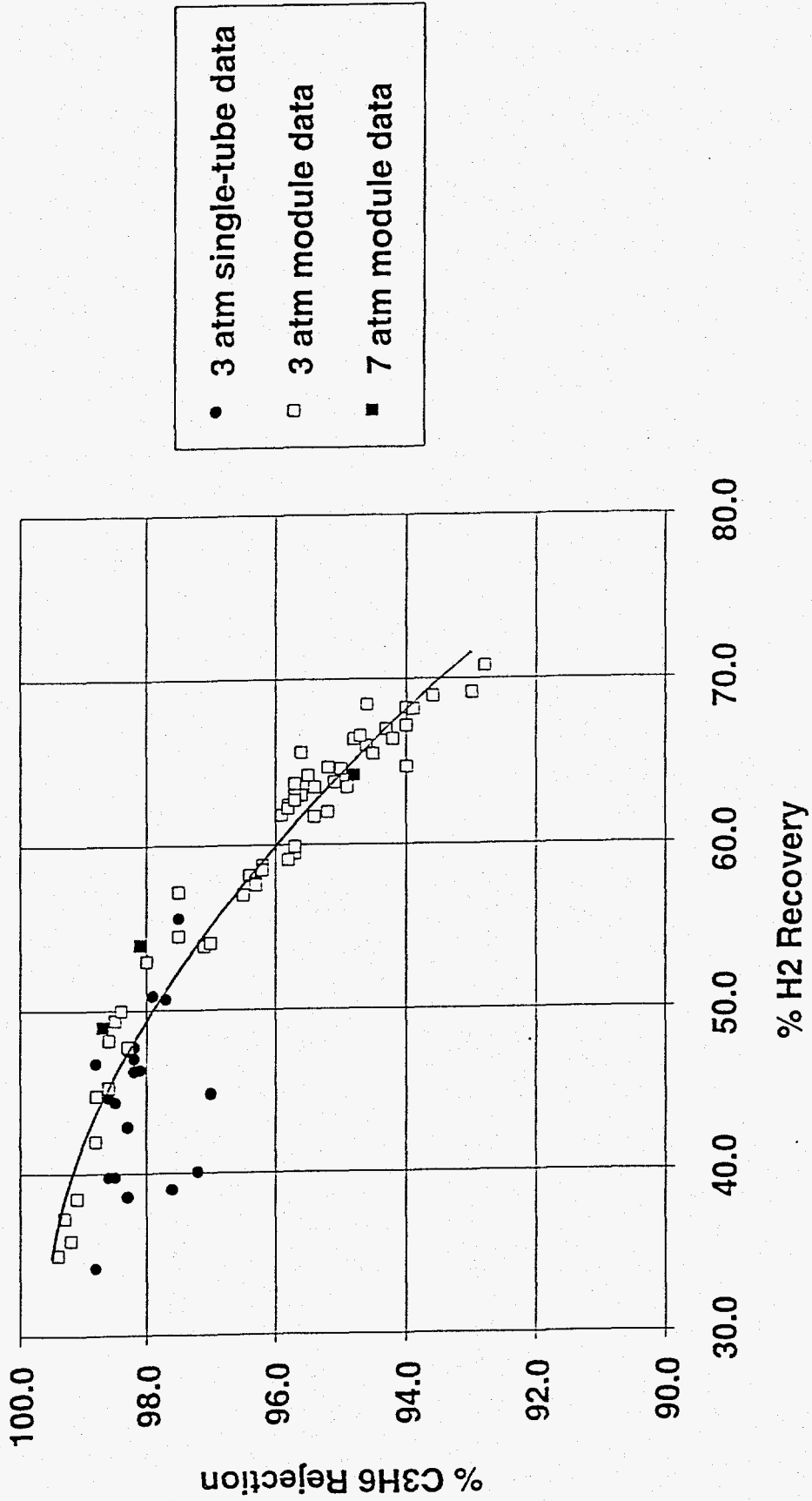
Figure 28. Performance of Multi-tube Module at 3 and 7 atm Feed Pressure: H₂ Recovery vs Propylene Rejection

FCC Offgas: C3H8 Rejection vs. H2 Recovery
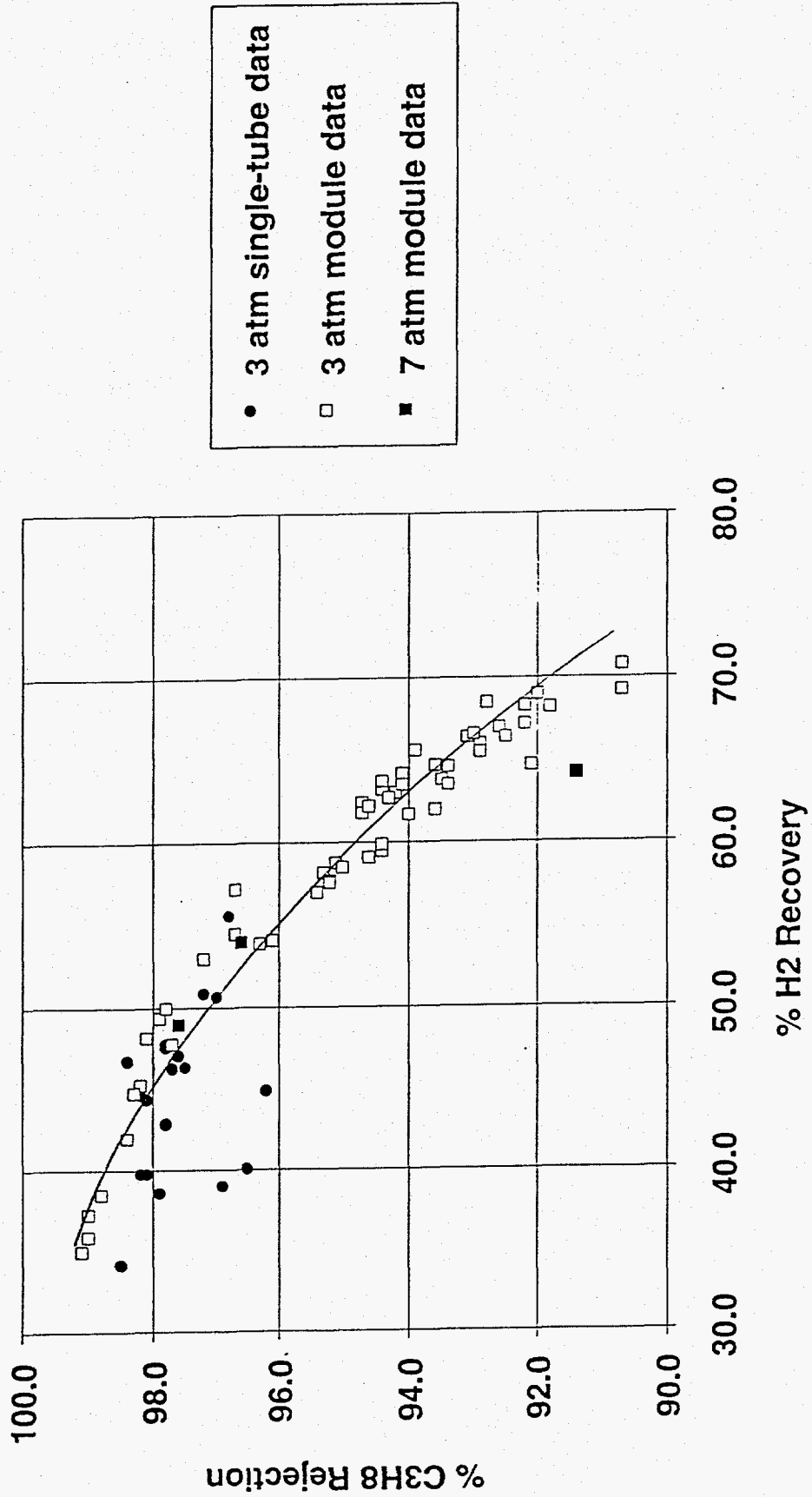
Figure 29. Performance of Multi-tube Module at 3 and 7 atm Feed Pressure H2 Recovery vs Propane Rejection

FCC Offgas: C2H4 Rejection vs. H2 Recovery
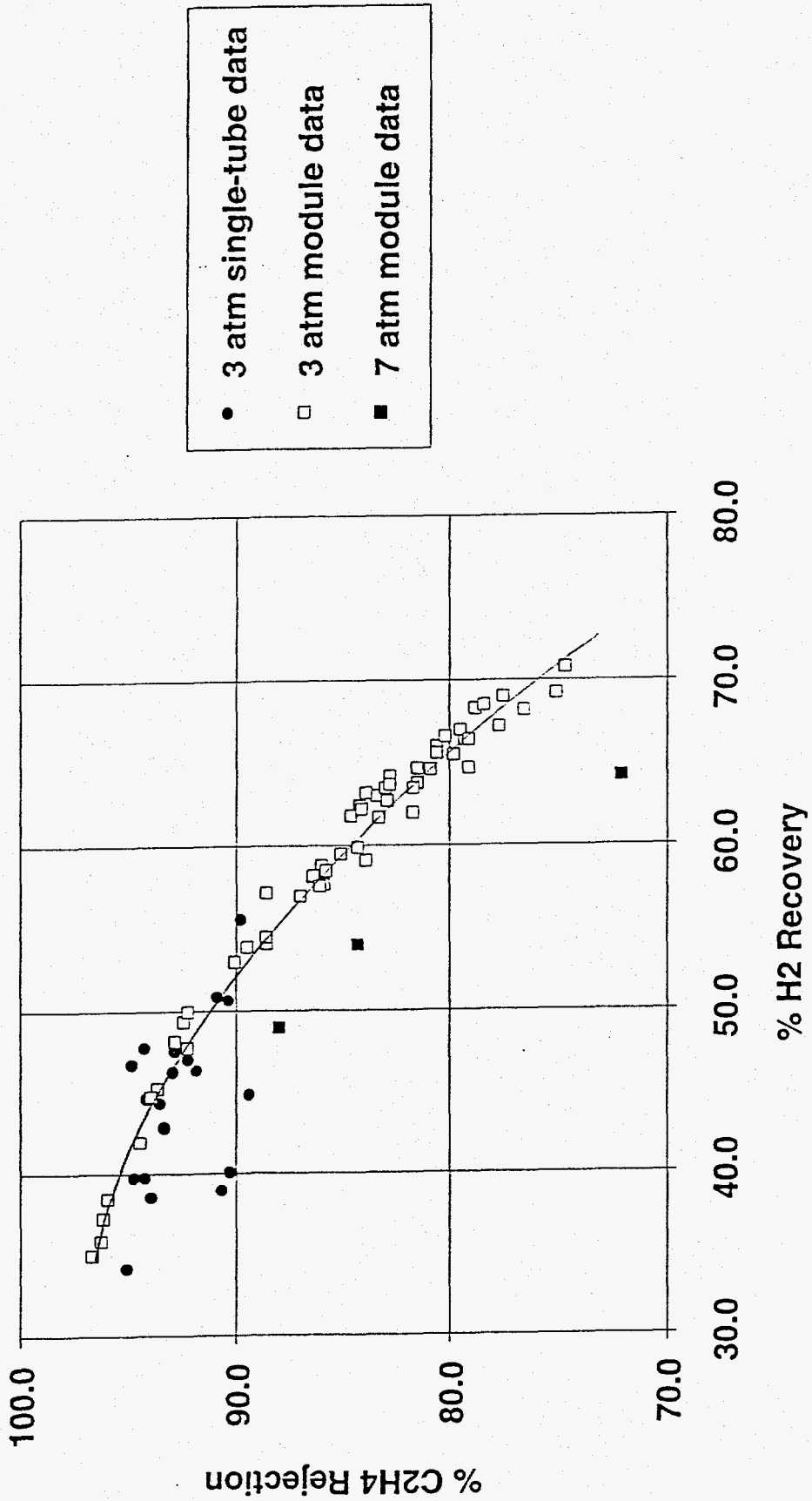
Figure 30. Performance of Multi-tube Module at 3 and 7 atm Feed Pressure H₂ Recovery vs Ethylene Rejection
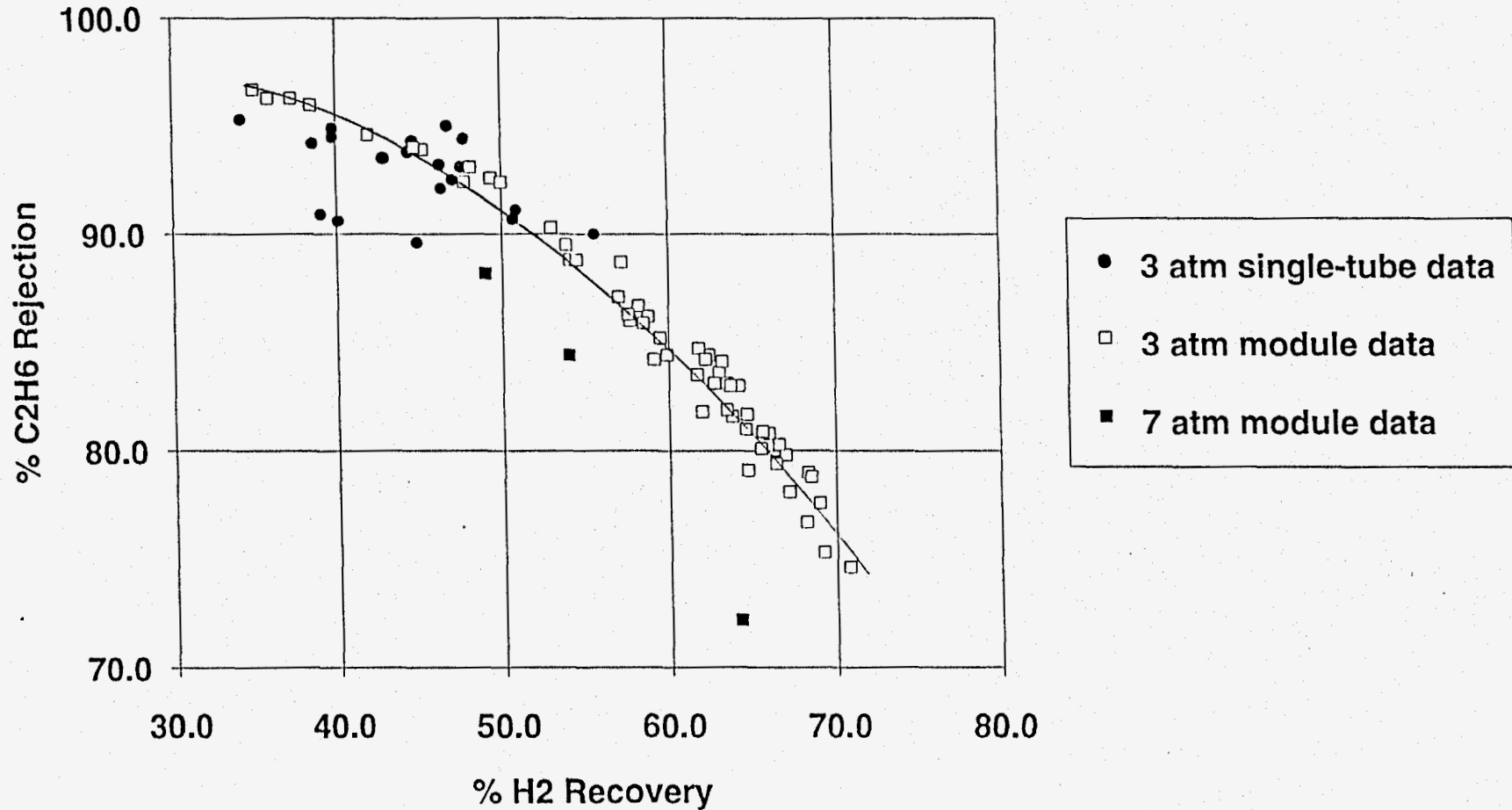
Figure 31. Performance of Multi-tube Module at 3 and 7 atm Feed
Pressure H_2 Recovery vs Ethane Rejection

FCC Offgas: CH4 Rejection vs. H2 Recovery
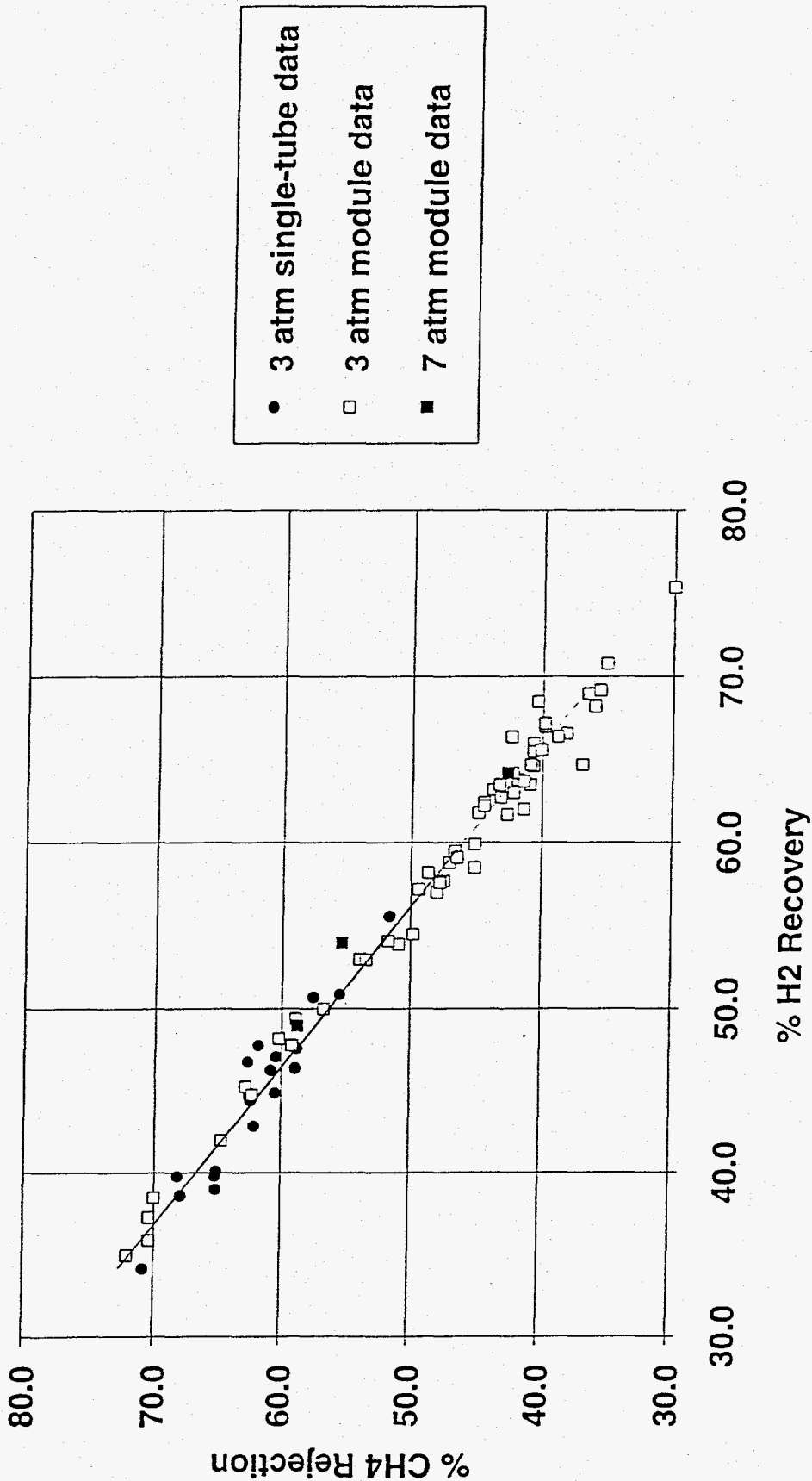
Figure 32. Performance of Multi-tube Module at 3 and 7 atm Feed Pressure H2 Recovery vs Methane Rejection

FCC Offgas: A/F vs. H2 Recovery
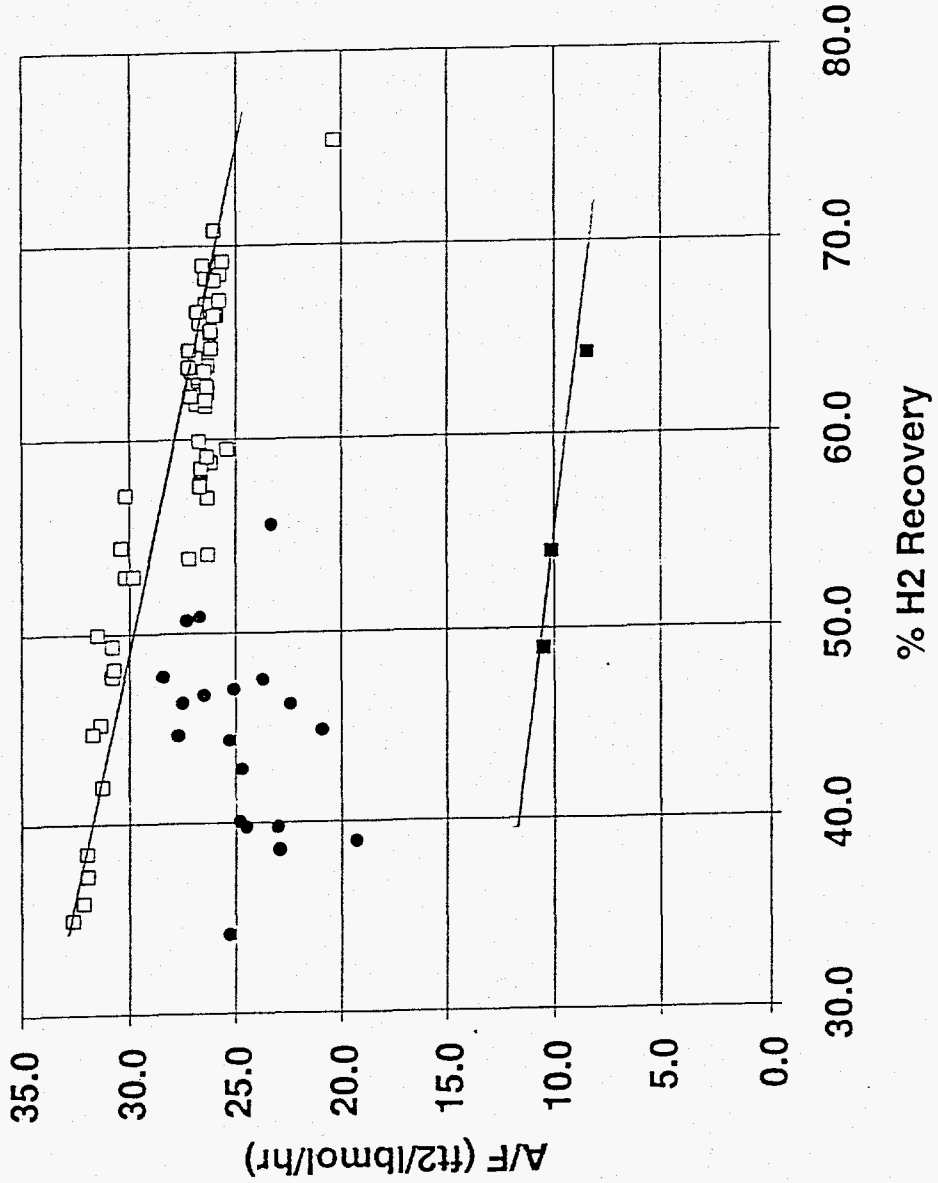
Figure 33. Performance of Multi-tube Module at 3 and 7 atm Feed
Pressure H₂ Recovery vs A/F

FCC Offgas: H2 mol fraction in HP effluent vs. H2 Recovery

Figure 34. Performance of Multi-tube Module at 3 and 7 atm Feed Pressure H2 Recovery vs H2 Mole Fraction in High Pressure Effluent

FCC Offgas: Total C3 mol fraction in HP effluent vs. H2 Recovery
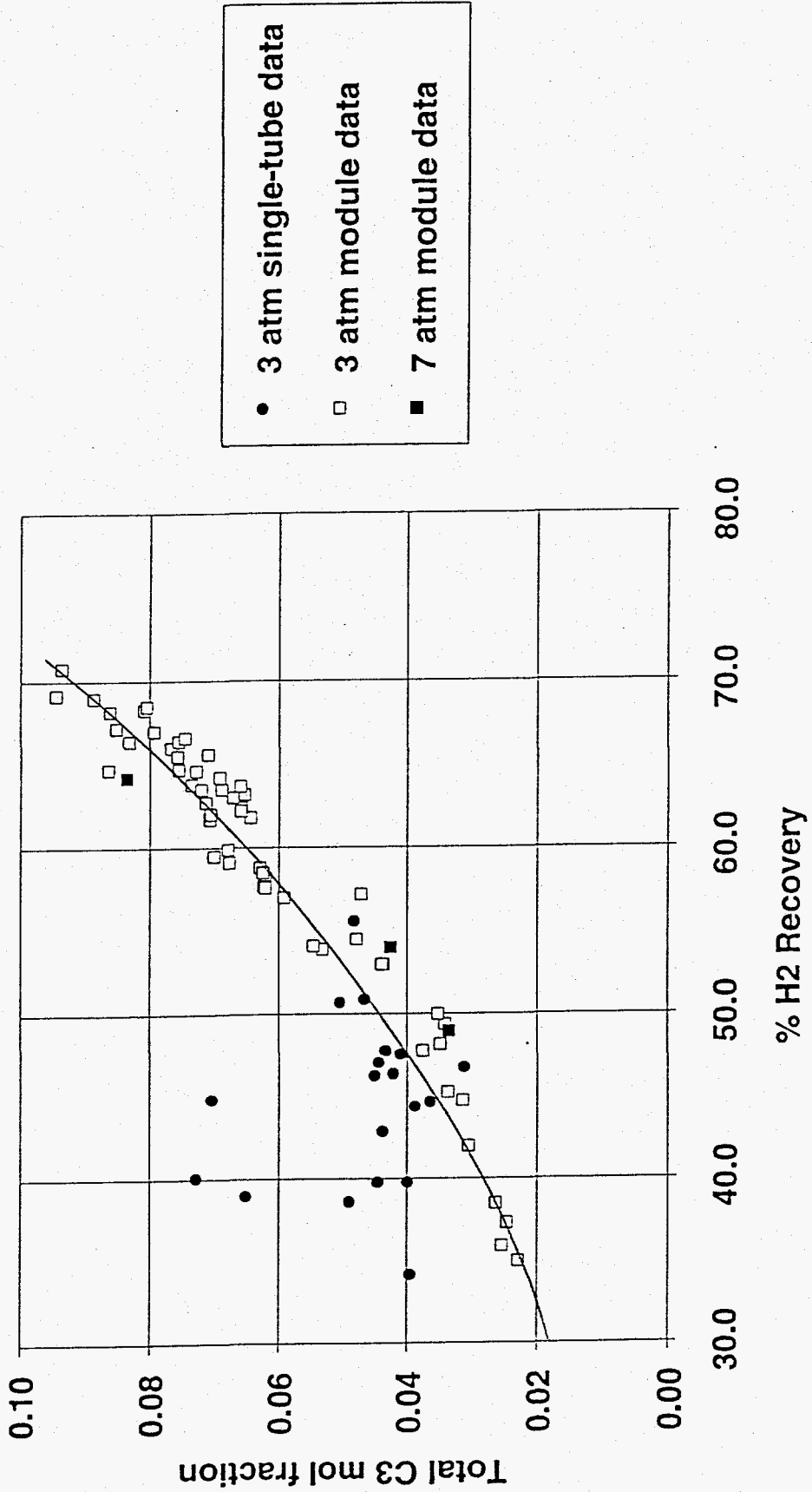
Figure 35. Performance of Multi-tube Module at 3 and 7 atm Feed Pressure H_2 Recovery vs Total C_3 Mole Fraction in High Pressure Effluent

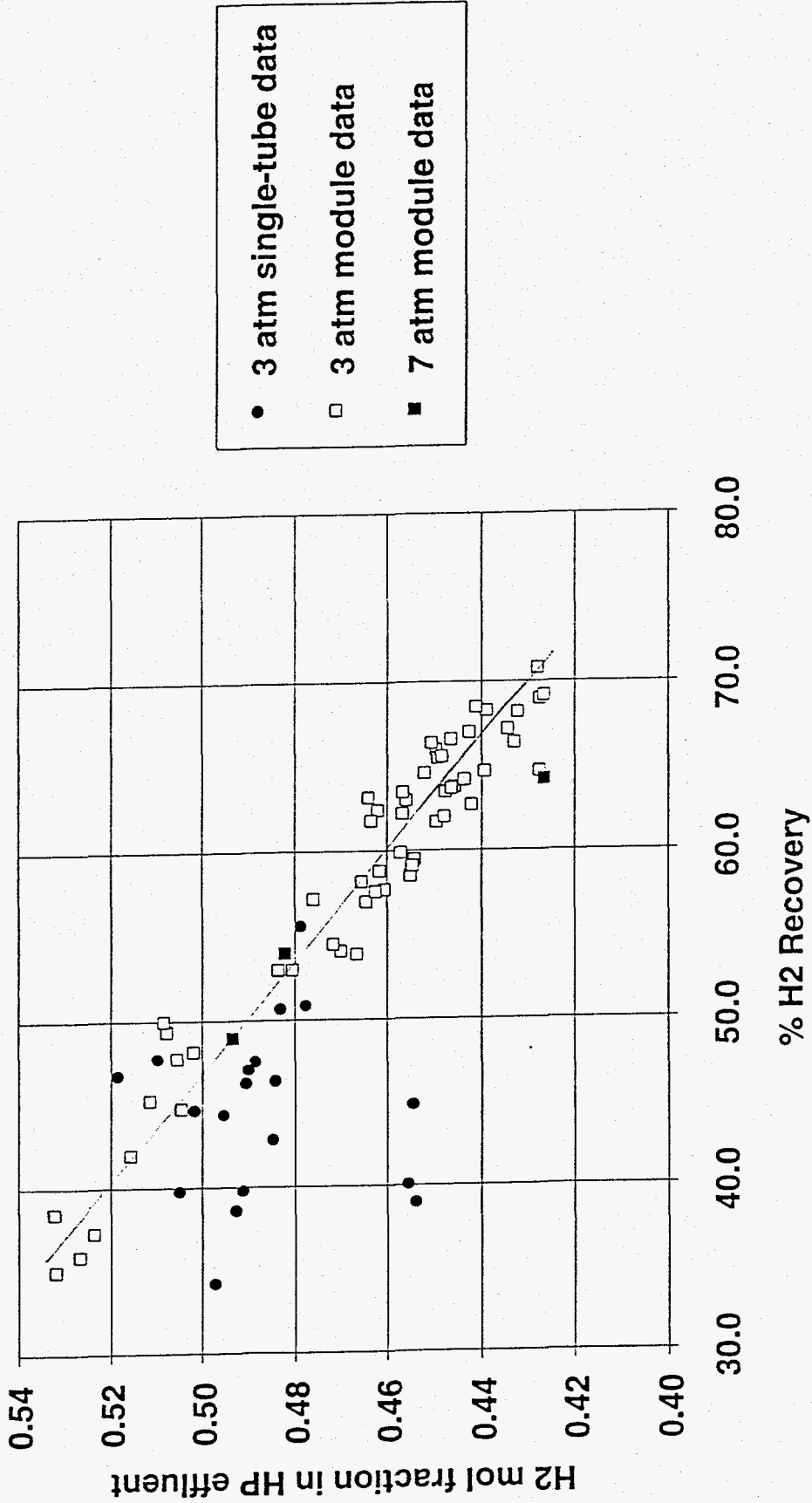### 3.9.3 Effects of Temperature, Feed Flow Rate and Feed Pressure

During the 2-month test period, the effects of variation in feed flow rate and membrane operating temperature were also investigated for the separation of hydrogen from hydrocarbons with the FCC mix.   The results are shown in **Figure 36**.   At a constant flow rate, a temperature change from 296 K to 306 K caused hydrogen recovery to decrease from 68% to 53% while concomitantly increasing the propylene rejection from 94% to 97%. Importantly, changes in temperature of this magnitude did not move the performance off the recovery-rejection curve but moved along the performance curve. The effect of temperature on moving from an operating point is not an unexpected result recognizing that the membrane separates by adsorption and surface diffusion through the pores of the carbon membrane. The effect of temperature on conventional pressure swing adsorption (PSA) used for separation of gases is of a similar nature and magnitude.

The effect of change of feed flow rate on the membrane operating point is also shown in **Figure 36.** Changing the feed flow rate has the same effect as the temperature i.e., it moves the membrane operating point along the same recovery-reject curve. A feed flow rate change (reduction) of 20% is required to decrease the hydrogen recovery from 68% to 53% while simultaneously increasing the propylene rejection from 94 to 97% with this FCC gas mix. The effect of feed pressure on membrane separation characteristics is shown in **Figures 28-35**. The data show that the membrane separation properties are only slightly affected at an elevated presssure (7 atm) with the FCC mixture, but the membrane area is decreased by 65-70% by increasing the pressure from 3 to 7 atm.

3.9.4 Effect of Feed and Sweep Directions on the Membrane Performance

The feed to the membrane module can be from the bottom or the top of the module.   The sweep flow directions can be appropriately changed to be either co-current or counter-current.   The effect of feed from the top or the bottom for the separation of the FCC mix was investigated.   The data indicated that the preferred direction of feed is from the membrane bottom as it improves the membrane separation properties.

Sweep flow with the FCC mix was changed from counter-current to co-current. The data indicate that counter-current sweep is preferred.   The observations are similar to those in the operation of heat exchangers where counter-current flow allows the maximum temperature driving force for heat exchange.

3.10 SSF Membrane Characteristics : Tubes vs Sheets

The benchmark performance data for the SSF membrane coated on carbon sheets was shown in **Figures 2-5** and that for tubes has been discussed in the previous sections of this report. The key differences between the two are :

MIXCHART.XLS Chart 94

FCC Mixture: C3H6 Rejection vs. H2 Recovery
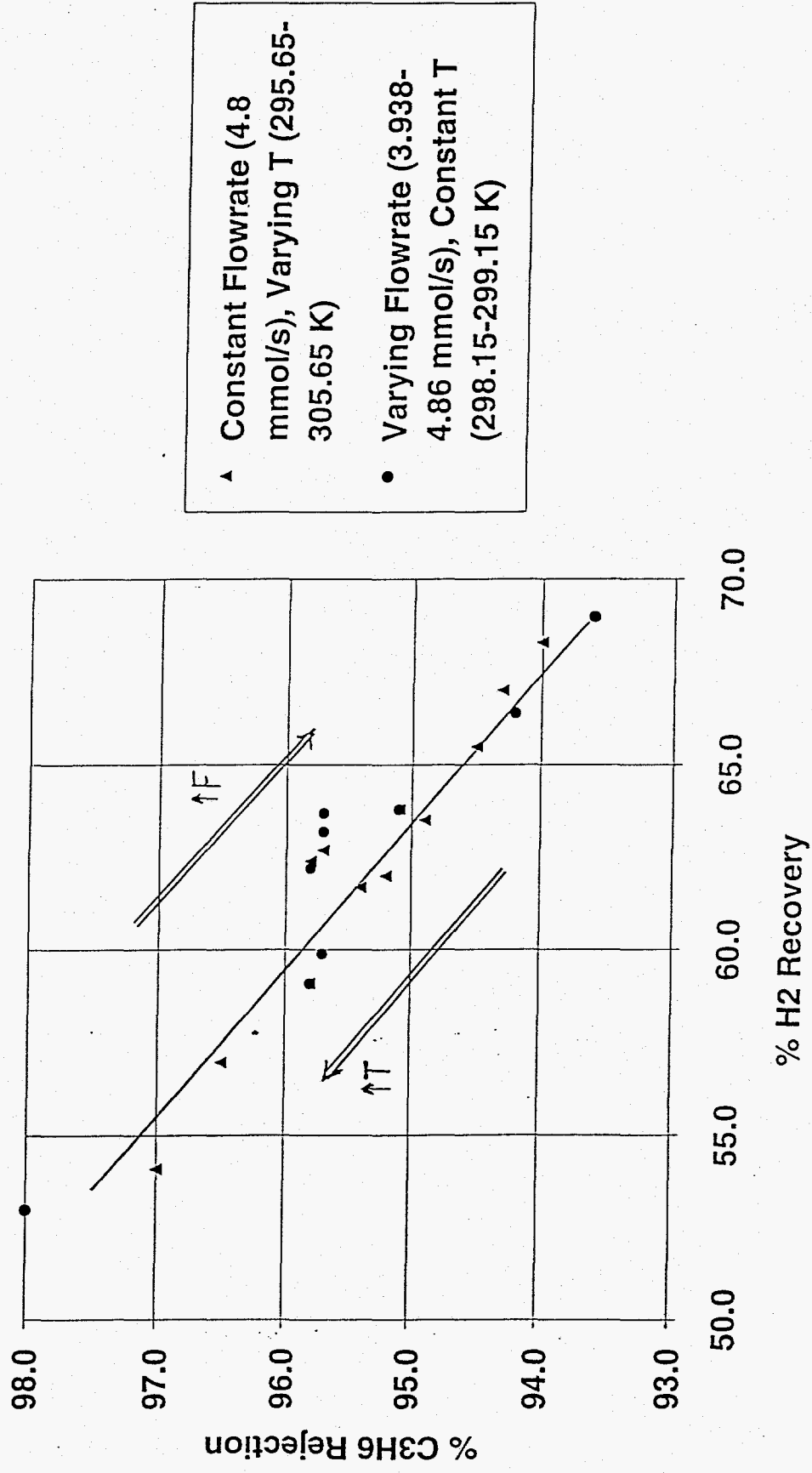
Figure 36. Effect of Temperature and Flow Rate on Membrane Performance

(i) The tubular membrane has a significantly lower (5-10 fold) membrane area required for the separation.

(ii) The rejections for C_2's and C_1's are higher for the tubular membrane (C_3 rejections are similar), resulting in an overall separation that is superior to that of the sheet membrane. This results in a higher enrichment of hydrogen in the high pressure effluent stream vs the sheet membrane.

Thus, the tubular SSF membrane encompasses both a selectivity and a permeability advantage over the sheet membrane. For Phase I of the program, the technical goals are therefore vastly exceeded.

4.0 PROCESS DESIGN, ECONOMICS AND ENERGY SAVINGS

4.1 Applications of SSF Membrane

The key features of the SSF membrane that drive the applications are :

(i) More selectively adsorbed species (i.e., larger molecules) are transported to the permeate side of the membrane.
(ii) The less selectively adsorbed species (i.e., smaller molecules) are enriched in the non-permeate stream and are thus recovered at feed pressure.
(iii) Large rejections of hydrocarbons are achieved while hydrogen from a H_2-hydrocarbon mixture is recovered.
(iv) The separations can be achieved at relatively low pressures (e.g., 3 atm feed pressure).
(v) The permeability through the membrane is large; thus the membrane area required for separation is small even at relatively low feed pressures.

While recognizing the above features of the SSF membrane and evaluating Air Products' business needs, the following initial applications were identified by business areas :

(a) **Recovery of hydrogen from refinery off-gas streams (U.S. Patent 5,354,547 (1994))**

(b) **Increased production of hydrogen from a existing hydrogen plant which uses a pressure swing adsorption (PSA) system for the production of pure hydrogen (99+ % purity) (U.S. Patent, 5,435,836 (1995))**

(c) **Fractionation of hydrocarbons (US Patent 5,332,424 (1994)).**

Patents have been procured for all of the above three processes where the SSF membrane is integrated with the rest of the process for new/increased hydrogen recovery.

Fractionation of hydrocarbons is not a part of this program and will not be discussed further.

4.2 Process Integrations and Economics for H_2 Recovery

4.2.1 Recovery of Hydrogen from Refinery Off-Gas Streams

Figure 37 shows the process scheme for the recovery of H_2 from a refinery off-gas stream. In the process, the waste gas at 50-200 psig is fed to an SSF membrane and the non-permeate stream enriched in H_2 (containing primarily H_2 and CH_4 and small amounts of C_2+s) is compressed (if necessary) to the PSA pressure; 99+ purity H_2 is recovered from the PSA at the PSA feed pressure. The PSA off-gas, consisting of all the hydrocarbons fed to the PSA and the unrecovered H_2, is either used as fuel directly or can be used to sweep the permeate side of the membrane. The permeate from the membrane is used as fuel or can be used further for hydrocarbon fractionation. In the evaluation of the overall process, a methane/natural gas stream is added to the permeate fuel stream to compensate for the hydrogen removed from the off-gas which would otherwise be used as fuel.

Often in refineries, the off-gas may be available from a fuel header or from a specific process (e.g., fluid catalytic cracker) which may contain a variety of contaminants such as large hydrocarbons (e.g., C_6+). These contaminants can be removed in a conventional activated carbon temperature swing adsorption (TSA) system. Additionally, it may be necessary to compress the permeate stream to a fuel header pressure if the fuel cannot be used at the low permeate pressure. These optional additions to the process are also shown in **Figure 37**.

A process design was carried out for the recovery of 1 MM scfd (million standard cubic feet per day) of hydrogen from the "standard" FCC stream containing 20% H_2 (used as the benchmark test stream in this work), the details of which are shown in **Figure 38**. The process design data were used for first pass economic analysis, the results of which are summarized in **Table 14**. The analysis indicates that the capital cost for hydrogen recovery is reduced by 50% and the energy cost by 15% by recovering H_2 from the above waste stream vs on-purpose production of hydrogen by steam-methane reforming. The total hydrogen cost is about 65% of that for hydrogen recovery by steam-methane reforming at this production volume.

It should be pointed out that the above FCC composition merely represents an FCC off-gas composition. A wide range of compositions (H_2 from 10 to 45%) and pressures are available as FCC and refinery off-gas streams. The process design, amount of hydrogen recovered and the economics vary significantly over the range of conditions. Thus, each stream needs to be evaluated for membrane performance, overall process design and economic evaluation.

Process Flow Diagram for
Typical SSF Application in Hydrogen Recovery

H2 Product

To refinery fuel gas header

60 psig

PSA Tail gas (to fuel) 5 psig

H2 PSA Unit

SSF non-permeate enriched in H2

SSF Membrane Unit

SSF Permeate (to fuel) 5-10 psig

5 psig

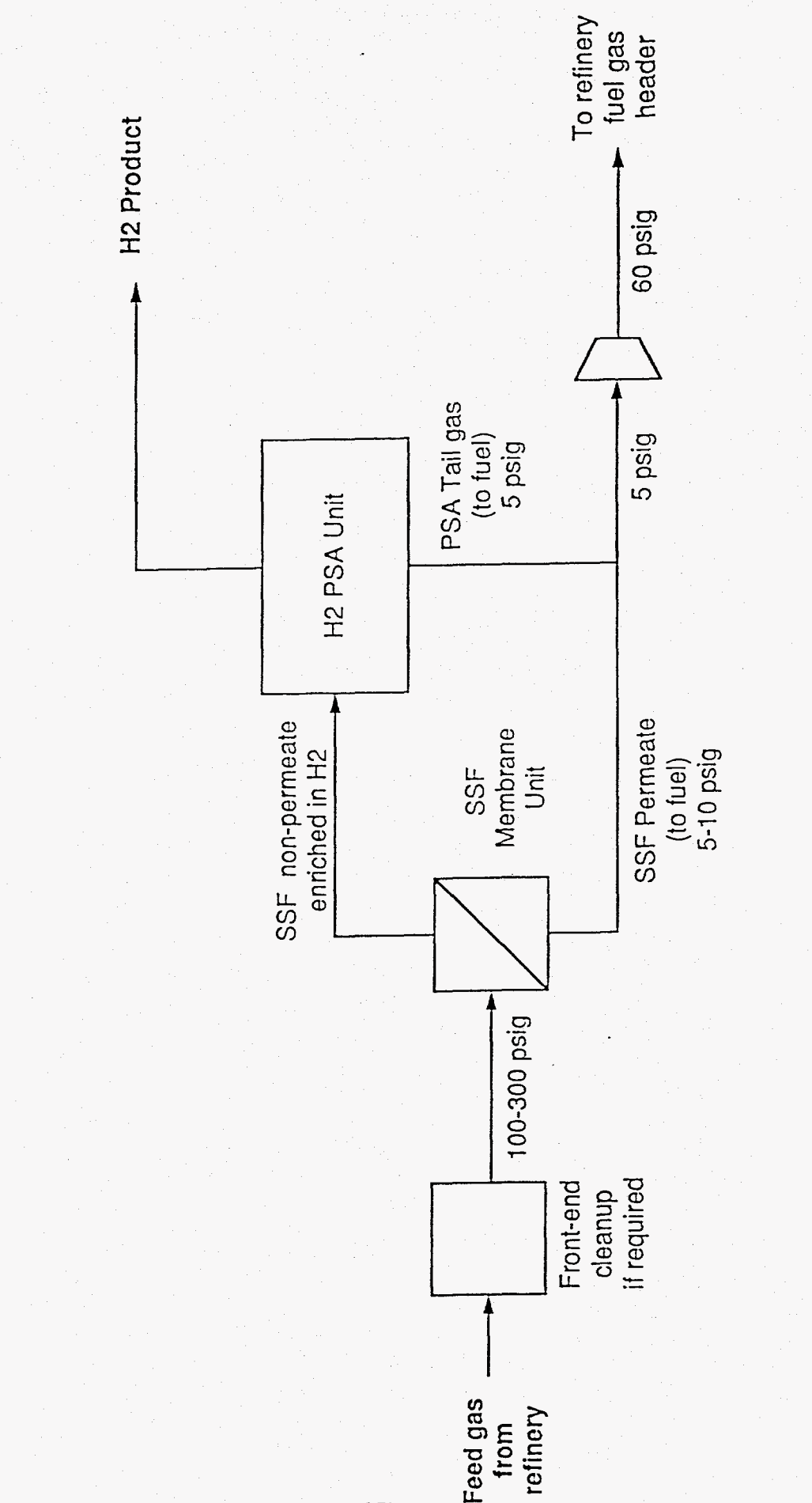100-300 psig

Front-end cleanup if required

Feed gas from refinery

Figure 37. Process Flow Diagram for Recovery of H₂ from Refinery Off-Gas Stream

15b

Hydrogen Recovery from Refinery Waste Gases

FCC Offgas

13.2 MMSCFD Feed

20% H_2 , 20% C_1, 8% C_2, 8% C_2 =

15% C_3, 29% C_3 =

P = 100 psig

SSF Membrane-PSA Hybrid

Tubular membrane

49.7% H_2

200 psig

SSF Membrane

H_2 PSA

1 MMSCFD
99+% H_2

CH_4 Make up

PSA Reject

to Fuel
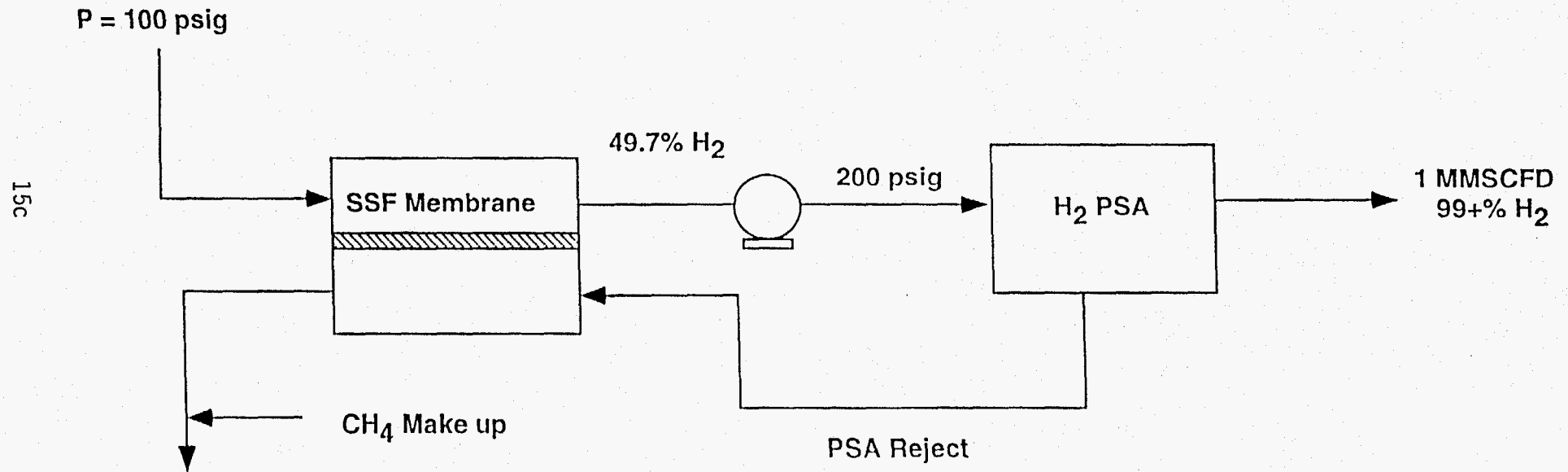
Membrane Area = 25,500 ft^2

Hydrogen Recovery = 62.0%

Rejection

Methane = 54.0%

Ethane = 85.3%

Ethylene = 83.0%

Propane = 97.2%

Propylene = 98.6%

15c

Figure 38. Process Flow Details for Recovery of H_2 from Refinery
FCC Off-Gas Stream

TABLE 14

Cost Analysis for Hydrogen Recovery from Refinery Waste Streams

Product : 1 MM SCFD Hydrogen at 200 psig and 99.9% Purity

Waste Stream at 100 psig, containing 20% H2, 20% C1, 16% C2, 44% C3

15d

Case	Capital	Energy	Total H2 Product Cost
SSF / PSA	0.50	0.86 *	0.65
SMR / PSA	1.00	1.00	1.00

* Includes CH4 Make-up to Refinery Fuel System @ $2.50 / MMBTU ; 97% Onstream

4.2.2 Improved H_2 Recovery in H_2 Plants

The most prevalent H_2 production technology involves reforming of methane with steam followed by recovery of pure hydrogen (99+%) using a H_2 PSA.   The recovery of H_2 in a PSA is typically about 80% (it is affected by product purity, feed pressure, and feed composition).   The H_2 in the PSA waste stream (along with small amounts of methane and carbon monoxide) is typically used as low pressure fuel in the reformer burners.

Figure 39 shows the integration of the SSF membrane in this process for increased production of hydrogen.   In the process, the PSA off-gas containing H_2, CO_2, CH_4 and small amounts of CO and N_2 is fed to the SSF membrane. The membrane preferentially permeates CO_2, CH_4 , CO and N_2 while enriching H_2 in the non-permeate stream.   The H_2-enriched stream is compressed and recycled to the PSA,thus increasing the total H_2 fed to the PSA and hence increasing the overall recovery of H_2 in the plant. It is thus possible to increase the overall H_2 recovery from 80% to 90%.   This concept is useful in debottlenecking existing H_2 plants or in reducing the reformer size in new plants.

Process design data for this scheme are being generated. The design and economics will be presented in the next report.

4.3 Energy Savings and Emissions Reduction

Energy and waste reductions by implementation of SSF/PSA technology were estimated.   The following basis was used for calculation of the energy savings in the year 2010 :

Volume of H_2 recovered :

1. 1100 MM scfd H_2 available in waste gas streams
2. 50% implementation of SSF/PSA technology
3. 45% of H_2 in waste gas recovered
4. Volume of H_2 recovered ~250 MM scfd

Energy Basis for Comparison :

1. Current technology : SMR/PSA
2. Energy to produce H_2 by SMR/PSA = 420 BTU/scf
3. Energy saving = 15% by SSF/PSA
4. Heating value of CH_4 = 1000 BTU/scf
5. Heating value of H_2 = 320 BTU/scf

SSF-PSA Hybrid for Enhanced H2 Recovery in H2 Plants
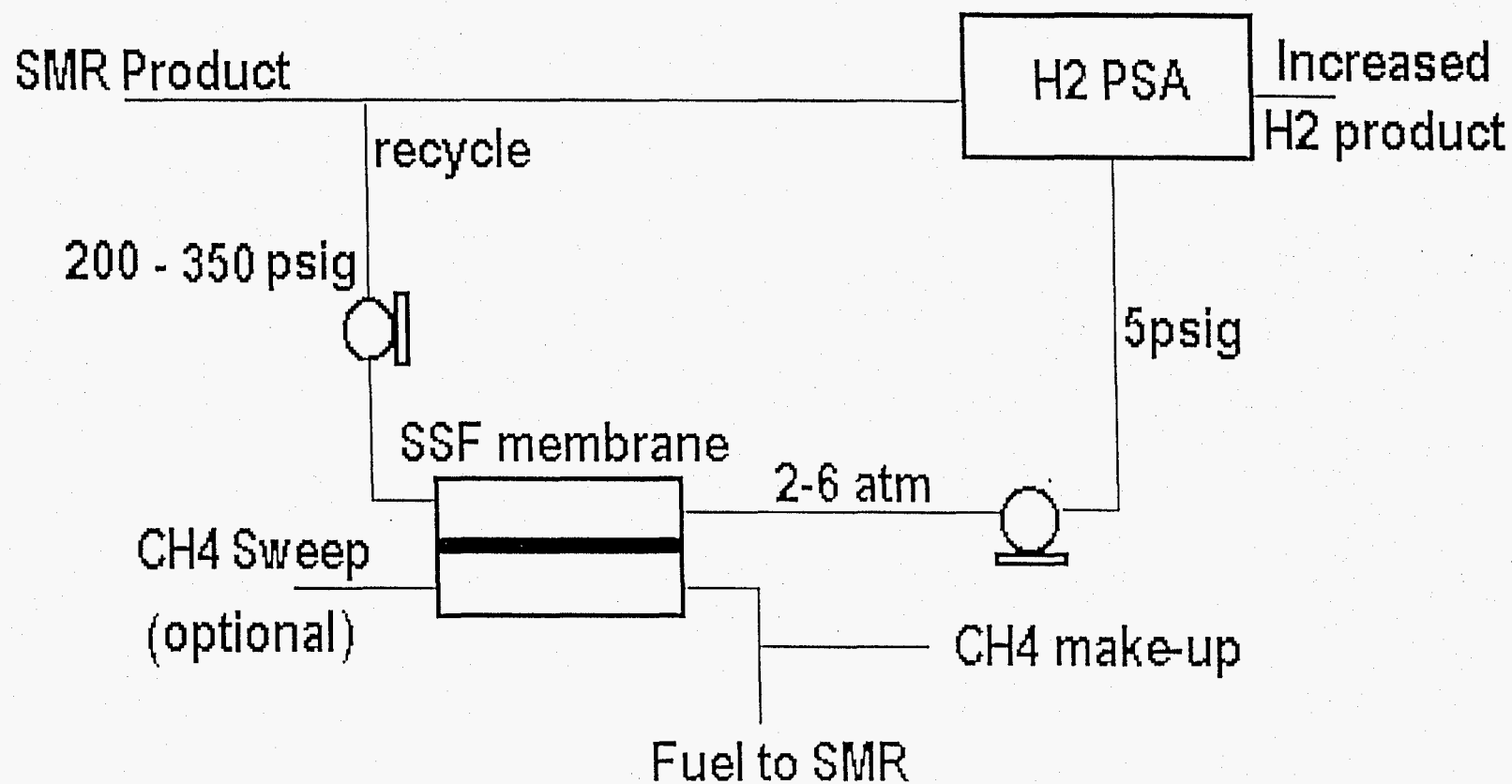
Feed : H2 (23-49%) +CO2+CH4+CO; 2-6 atm feed pressure

Figure 39. SSF-PSA Hybrid for Enhanced Hydrogen Recovery in H2 Plants

Waste Basis for Comparison :

1. H_2 combustion produces ~ 10 lb NO_x / 1 MM scfd H_2 by SMR/PSA
2. CO_2 production by oxidation of methane : 1 mole CO_2 / mole CH_4

Table 15 summarizes the energy and waste savings for recovery of H_2 by SSF/PSA vs on-purpose manufacture by steam-methane reforming.   Process design for recovery of H_2 by SSF/PSA with the above FCC mix showed a 15% reduction in energy requirement for the SSF/PSA process.   In this analysis is included the methane replacement energy assuming that the stream is being used as fuel and hence the H_2 extracted from the stream needs to be replaced by an equivalent amount of CH_4 to equal the fuel value of the stream.   In some cases, the fuel may have no value (may be flared or used to make steam for venting at some refineries on the U.S. East Coast in the summer), and hence the energy savings and emissions reductions are significantly greater, as shown in Table 15.

5.0 SUMMARY

In the first phase of the exploratory development work in the scale-up of SSF membranes, the following was achieved :

(i) A low cost alumina tube was developed with a tube supplier for coating the SSF membrane.

(ii) A reproducible coating process was developed for SSF membrane preparation.

(iii) Membrane separation and permeability properties were exceeded vs the benchmark with sheet membranes, and these levels were 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 on the multi-tube module was generated 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 investigated 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.

TABLE 15

PROJECTED ENERGY AND WASTE SAVINGS IN YEAR 2010

BASIS : 250 MM scfd H_2 in year 2010

	Current Technology	Proposed Technology	Annual Savings in 2010
Description		.	
Energy :			
(i) w/CH_4 make-up	420 BTU/scf 79590 BTU/lb	357 BTU/scf 67650 BTU/lb	5.6×10^{12} BTU
(ii) w/o CH_4 make-up		37 BTU/scf	33.9×10^{12} BTU
Waste :			
CO_2	2.2×10^6 T/yr		
(i) w/CH_4 make-up		1.88×10^6 T/yr	0.32×10^6 T/yr
(ii) w/o CH_4 make-up		0.18×10^6 T/yr	2.0×10^6 T/yr
NO_x			
	10 lb/MM scf H_2	0	440 T/yr

6.0 REFERENCES

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7.0 ACKNOWLEDGEMENTS

APPENDIX I

Phase I Program Plan and Milestones

1. Program Project Identification Number	2. Program/Project Title
DE-FC04-93AL94461	Novel Select Surface Flow (SSF) Membranes for the Recovery of Hydrogen from Waste Gas Streams

3. Performer (Name, Address)	
Air Products and Chemicals, Inc. Corporate Science and Technology Center 7201 Hamilton Blvd. Allentown, PA 18195-1501	4. Program/Project Start Date **April 1 1993** 5. Program/Project Completion Date **May 31 1997**

8. Program/ Project Duration — Phase 1 1993 — 1994

6. Identification Number	7. Planning Category (Work Breakdown Structure Tasks)	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	9. Comments (Notes, Name of Performer)
1.1	Membrane Fabrication Scale-up																△				
1.1.1	Screen Hollow Tubes for Coating											▽									
1.1.2	Define Coating Techniques													▽							
1.1.3	Design/Construct Module Test Unit	▽								▽											
1.1.4	Design /Construct Tubular Module								▽								△				
1.1.5	Design/Construct Coating Apparatus														▽						
1.1.6	Fabricate Tubes for Modules																				
1.2	Tubular Membrane Performance																			→	
1.3	Testing for FCC Gas Monolith Coating and Performance																			▽	
1.4	Module Performance Testing																			▽	
1.5	Technical and Economic Feasibility Demonstrated																			△	

10. Remarks

11. Signature of Recipient and Date	12. Signature of DOE Reviewing Representative and Date
M-Anand Nov 23, 93	

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MILESTONES - PHASE I

Major Milestones

Δ   Consistent Membrane Target Properties Demonstrated (6/94)

Δ   Membrane Multi-tube Module Prepared (6/94)

Δ   Technical and Economic Feasibility Demonstrated (10/94)

Intermediate Milestones

∇   Membrane Tube selected (2/94)

∇   Coating Technique Defined (4/94)

∇   Module Test Unit Constructed (12/03)

∇   Module Housing Completed (10/93)

∇   Coating Equipment Constructed and Operational (3/94)

∇   Membrane Module Tests Completed (9/94)

∇   Coating of Monoliths Assessed (10/94)

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