Technology transfer to GTC was carried out, and with additional developments at GTC, the following were accomplished:

(i) Consistent alumina tube fabrication (control of pore size, porosity, tube interior surface finish, straightness),
(ii) Reproducible PVDC coating (specifications set on emulsion concentration, coating thickness),
(iii) Pyrolysis protocol (temperature profile and passivation conditions), and
(iv) Membrane QC (method and standard).

During this development, a significant improvement was made in the SSF membrane performance by improving the surface characteristics of the alumina tube interior. With this improvement, it is possible, for example, to increase the H_2 recovery from 50% to 62% while maintaining a 98% rejection of C_3's from the FCC H_2/hydrocarbon mixture.

The improved 3.5 ft long tubular membranes were prepared at GTC and tested with the standard FCC H_2/hydrocarbon mixture. The recovery-rejection curves are shown in Figures 21-23 for numerous individual 1 ft and 3.5 ft long tubes. The data show that:

(i) the SSF membrane preparation can be readily scaled from 1 ft to 3.5 ft long tubes,
(ii) the improvement in the 1 ft long tube can be translated into the 3.5 ft long tubes (not shown in Figures), and
(iii) there is a small increase in A/F associated with the improvement in membrane separation properties.

<u>3.4 Process Design, Economics and Waste Reduction:</u>

3.4.1 Recovery of Hydrogen from Refinery Off-gas Streams

Figure 1 shows the process scheme for the recovery of H_2 from a refinery off-gas stream. In the process, the waste gas at 50-300 psig is first fed to a temperature swing adsorption system (TSA) to remove trace contaminants that might foul the membrane. The gas is then fed to an SSF membrane unit. The non-permeate stream, enriched in hydrogen, (containing mostly H_2 and CH_4 with a small amount of C2's) passes into a PSA unit where 99+% H_2 is recovered at the nearly the original feed pressure. The PSA off-gas is combined with the low pressure permeate stream from the SSF membrane unit. The combined low pressure stream is compressed to 60 psig and returned to the refinery's fuel system. Methane or natural gas could be added to the returning stream to make up for the lost BTU content of the recovered hydrogen.

Air Products sponsored a marketing study by Wright-Killen and Associates to further clarify the size and potential content of the available waste gas streams that the SSF technology could treat. The refinery gases that we targeted for sources of H_2 were off-gases from FCC and hydrotreating units. Based on their report, a base case process such as the one described in the previous paragraph was developed to estimate the relative cost of hydrogen recovered by this method as compared to on-purpose H_2

Figure 21

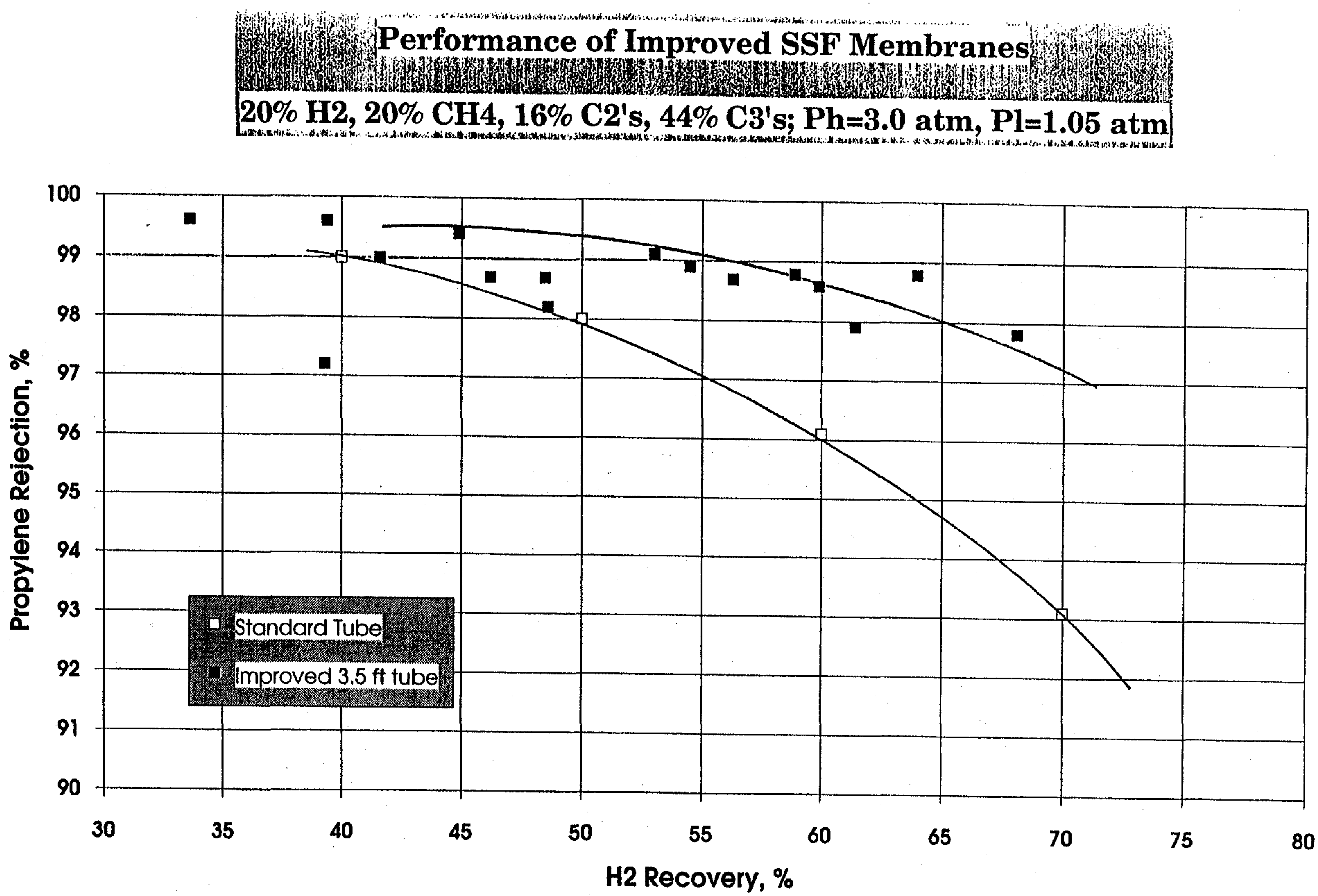
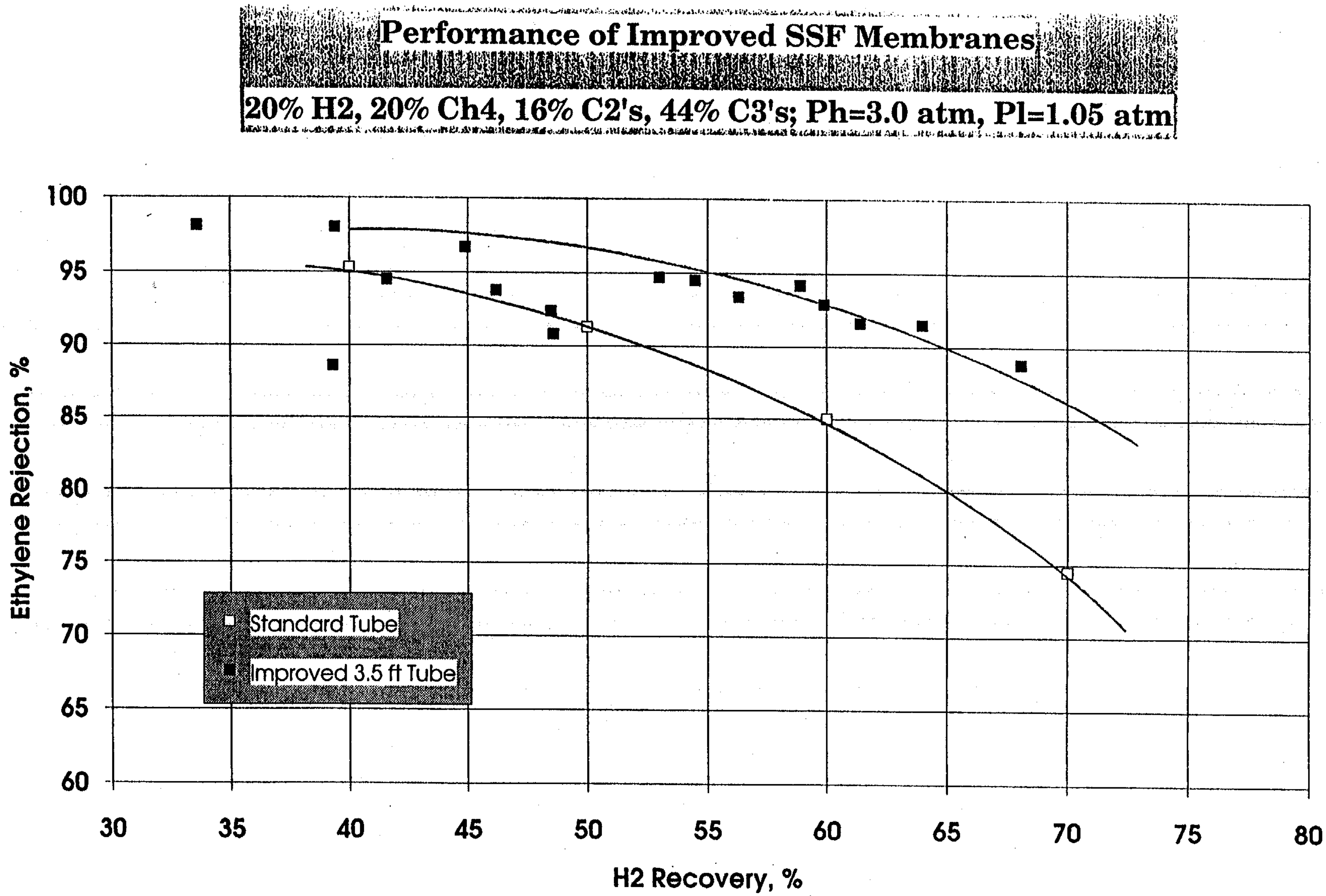
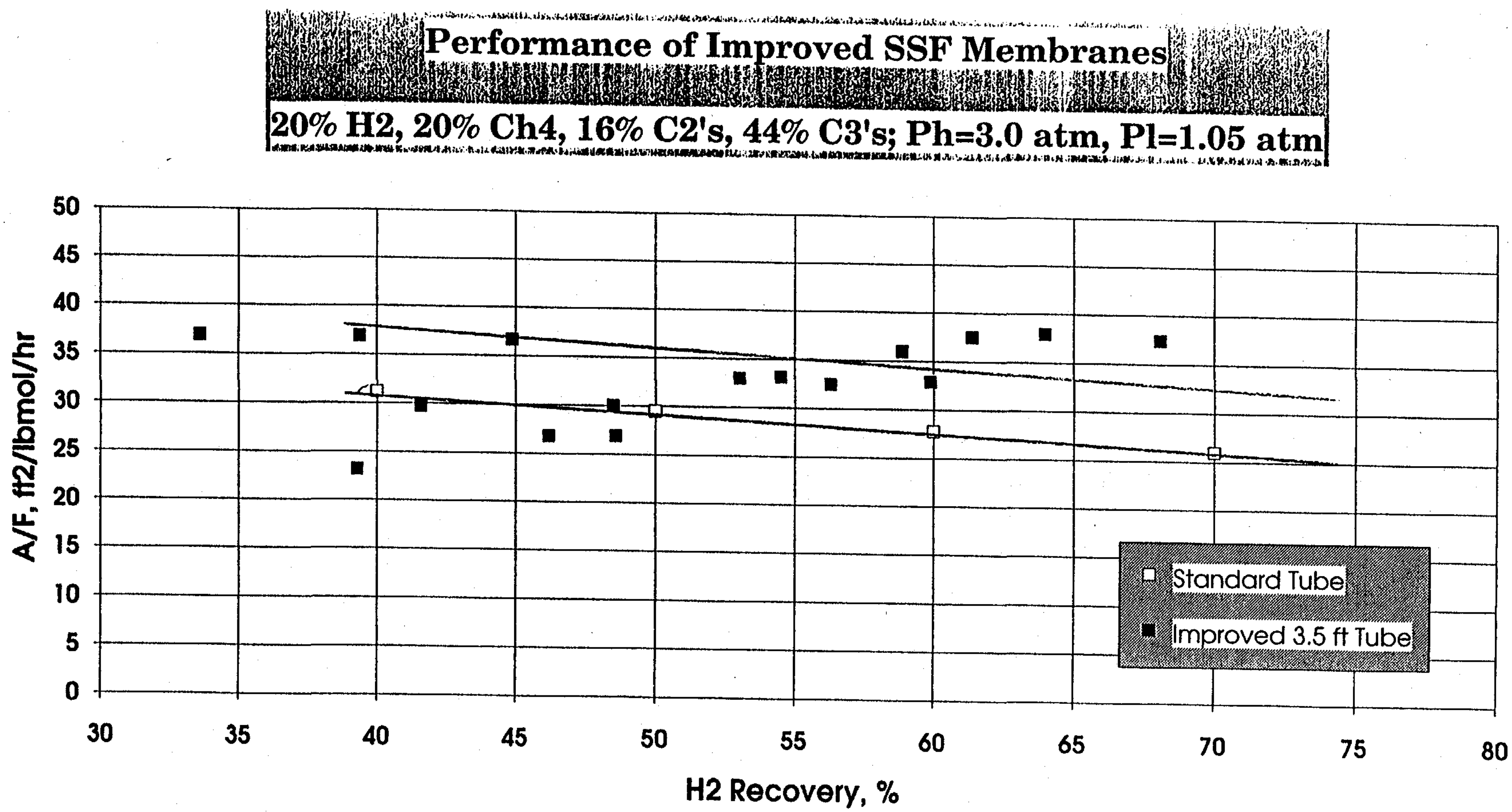

Performance of Improved SSF Membranes
20% H2, 20% CH4, 16% C2's, 44% C3's; Ph=3.0 atm, Pl=1.05 atm
Propylene Rejection, %
100
99
98
97
96
95
94
93
92
91
90
30
35
40
45
50
55
60
65
70
75
80
H2 Recovery, %
Standard Tube
Improved 3.5 ft tube

Figure 22



Performance of Improved SSF Membranes
20% H2, 20% Ch4, 16% C2's, 44% C3's; Ph=3.0 atm, Pl=1.05 atm
100
95
90
85
80
75
70
65
60
Ethylene Rejection, %
30
35
40
45
50
55
60
65
70
75
80
H2 Recovery, %
Standard Tube
Improved 3.5 ft Tube

Figure 23



Performance of Improved SSF Membranes
20% H2, 20% Ch4, 16% C2's, 44% C3's; Ph=3.0 atm, Pl=1.05 atm
A/F, ft2/lbmol/hr
50
45
40
35
30
25
20
15
10
5
0
30
35
40
45
50
55
60
65
70
75
80
H2 Recovery, %
Standard Tube
Improved 3.5 ft Tube

production by current technology. The composition that best represents the portion the waste refinery gas market the SSF membrane could address is listed in Table 2. The feed gas is expected to be available at an average pressure of 220 psig and ambient temperature. The average fuel gas header pressure in this market was found to be about 60 psig.

Table 2
Average Composition of FCC Waste Gas Stream

Gas	Volume Fraction
Hydrogen	35%
Methane	30%
C2's	24%
C3's	7%
Other	4%

The typical application would treat 25 MM scfd (million standard cubic feet per day) of feed gas and produce 5 MM scfd of 99+% hydrogen. For this base case economic study, we assumed that the fuel value of the hydrogen recovered from the waste gas stream was valued at $2.10/MM BTU. Capital cost estimates for all the major pieces of process equipment were based on vendor estimates. Project execution and equipment installation charges were also included.

Table 3 lists the results of the comparative economic analysis for a typical application producing 5 MM scfd of hydrogen. It should be noted that the energy savings estimate has decreased from 15% in Phase I to 13% now. The reasons for this are : (i) permeate recompression to fuel header pressure and (ii) TSA for cleaning of the feed gas.

3.4.2 Energy Savings and Emissions Reductions

Energy and waste reduction by implementation of the SSF/PSA technology were estimated. Based on our recent marketing information, we used the following to calculate energy saving in the year 2010.

Volume of Hydrogen Recovered

1. 1800 MM scfd H_2 available in waste gas in the US
2. 40% of the gas is amenable to recovery using SSF/PSA
3. 56% of the contained H_2 is recovered
4. Volume of H_2 recovered ~400 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 = 13% by SSF/PSA
4. Heating value of CH4 = 1000 BTU/scf; H_2 = 320 BTU/scf

Table 3

Cost Analysis for Hydrogen Recovery from Refinery Waste Gas

Product: 5 MM SCFD Hydrogen at 200 psig and 99.9% purity
Waste Stream at 220 psig containing 35% H_2, 30% C_1, 24% C_2, 7% C_3

Case	Capital	Energy	Total H_2 Product Cost
SSF/PSA	0.5	0.87*	0.66
SMR/PSA	1.0	1.00	1.00

*Includes CH_4 make-up to refinery fuel system

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Waste Basis for Comparison

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

Table 4 summarizes the energy and waste savings for recovery of H2 by SSF/PSA vs. on-purpose H2 production by steam-methane reforming. The base case process for recovery of H2 with SSF technology uses 13% less energy than the SMR/PSA process. This comparison included a fuel credit for the excess steam produced in the SMR/PSA process. If there were no credit for this excess steam, the energy savings would be more than double the reported value.

4.0 SUMMARY

In Phase II, Technology Development, of the SSF membrane program, the following were achieved :

1. Design data was generated for two applications of the SSF membrane: (a) H_2 recovery from waste gas mixtures of H_2 and light hydrocarbons (C1-C4's) and (b) increased H_2 production in plants producing H_2 by steam methane reforming (SMR) followed by purification in a H_2 pressure swing adsorption (PSA) system. The data was generated with various feed gas mixtures at a wide range of pressures.

2. A 1 ft^2 membrane module was prepared and successfully tested in the field for two months. It was determined that : (a) the membrane separation properties measured in the field matched well with those measured in the lab, (b) the membrane was stable over the 2-month test, (c) a relatively constant composition product can be obtained with a varying feed composition by controlling the ratio of the high pressure effluent and the feed flow rates.

3. Technology for membrane preparation was transferred to GTC. 3.5 ft long tubular membranes have been prepared consistently at GTC. A significant improvement in membrane separation properties has been demonstrated in 3.5 ft long tubes. This results in higher hydrogen recovery and an overall lower cost for the separation.

4. A study was undertaken at Wright Killen Associates to define the gas streams and the size of the opportunity for H_2 recovery from FCC off-gas streams. Cost analysis was carried out with an average composition defined from the above study. Our analysis indicates a 34% lower cost and a 13% energy saving for H_2 recovery vs on-purpose H_2 production at a produc volume of ~ 5 MM scfd H_2.

5. Energy savings of 7.8 - 55.8 x 10^{12} BTU/yr are estimated for H_2 recovery via the SSF-PSA route for year 2010. CO_2 emission reductions are estimated at 0.2-2.8 T/yr and NO_x by 700 T/yr for year 2010.

6. All the milestones for Phase II were accomplished on time and within budget.

Table 4

PROJECTED ENERGY AND WASTE SAVING IN YEAR 2010

BASIS: 400 MM scfd H_2 in year 2010

Description:	Current Technology	Proposed Technology	Annual Saving in 2010
Energy:			
i) w/ CH_4 make-up	420 BTU/scf 79590 BTU/lb	365 BTU/scf 69170 BTU/lb	7.8×10^{12}BTU
ii) w/o CH_4 make-up		26 BTU/scf	55.8×10^{12}BTU
Waste			
CO_2:	3.5×10^6 T/yr		
i) w/ CH_4 make-up		3.3×10^6 T/yr	0.2×10^6 T/yr
ii) w/o CH_4 make-up		0.7×10^6 T/yr	2.8×10^6 T/yr
NOx:			
	10 lb/MM scf H_2		700 T/yr

5.0 REFERENCES

1. Anand, M, "Novel Selective Surface Flow (SSF^{TM}) Membranes for the Recovery of H_2 from Waste Gas Streams" Phase I: Exploratory Development; Final Report to Department of Energy, August 1995.

6.0 ACKNOWLEDGEMENTS

The technical work in Phase II of the work was done by M. Anand, J. Yang, T. Naheiri, K. Ludwig, G. Achilles, B.C. Louie, S. Wirth, R. Weber and K. Fabregas. The Wright Killen Study was carried out under the supervision of P.J. Cook. In addition, many ideas were contributed by S. Sircar and M.B. Rao. The contributions from B. Hart at Golden Technologies are also acknowledged.

Appendix I

Phase II Program Plan and Milestones

Phase II : Technology Development

Task 2.1 Perform Parametric Evaluation of SSF Membrane

- Determine performance of SSF membrane at different flow, pressure, temperature conditions in 1 ft^2 multi-tube module
- Develop design method for scaling up membrane to larger area
- Determine optimum operating conditions for membrane for H_2 separation application
- Determine membrane manufacturing partner and have scale-up
- Modify scale-up facility for preparing membrane and membrane housing
- Demonstrate membrane coating process on tubes
- Design housing and method for mounting tubes in commercial sized membrane modules
- Demonstrate "commercial" module design in small module (1-5 ft^2)
- Demonstrate membrane performance in above module
- Develop membrane QC procedures
- Prepare 1 ft^2 membrane and test in plant side-stream
- Determine if membrane needs to be protected from contaminants in plant side stream
- Estimate life of membrane in application and use for economic evaluation

Task 2.2 Optimize Design of Membrane

- Based on scale-up method develop, design commercial-scale SSF membrane-PSA hybrid system for H_2 recovery from FCC mix

Task 2.3 Perform Detailed Economic and Commercial Evaluation

- Perform economic evaluation with known cost of membrane
- Determine commercial feasibility jointly with APCI H_2 business area agreement in place

Task 2.4 Update Projections Develop Commercialization Plan

- Improve estimates of market potential
- Determine energy and waste reduction for opportunuities
- Determine commercialization timetable

Task 2.5 Project Management and Reporting

MILESTONES - PHASE II

Major Milestones

- Δ Key Process Parameters for Membrane Operation Defined (4/95)
- Δ Membrane Optimized for FCC Separation (10/95)
- Δ Commercial Evaluation Done (10/95)
- Δ Plant Evaluation Completed (10/95)
- Δ Process in Place with Scale-up Partner (10/95)

FORM EIA-459B
(10/80)

U.S. Department of Energy

FEDERAL ASSISTANCE MILESTONE PLAN

1. Program Project Indentification Number: DE-FC04-93AL94461

2. Program/Project Title: 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 2 — ◄ 1994 ► ◄ 1995 ►

6. Identification Number	7. Planning Category (Work Breakdown Structure Tasks)	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT							9. Comments (Notes, Name of Performer)
2.1	Parametric Evaluation of Membrane Done							△													
2.2	Optimize Design of Membrane													△							
2.3	Complete Economic/ Commercial Evaluation													△							
2.4	Update Projections and Commercialization Plan													△							
2.5	Project Management and Reporting																				

10. Remarks

11. Signature of Recipient and Date: M. Anand, Jan 5, 94

12. Signature of DOE Reviewing Representative and Date