(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

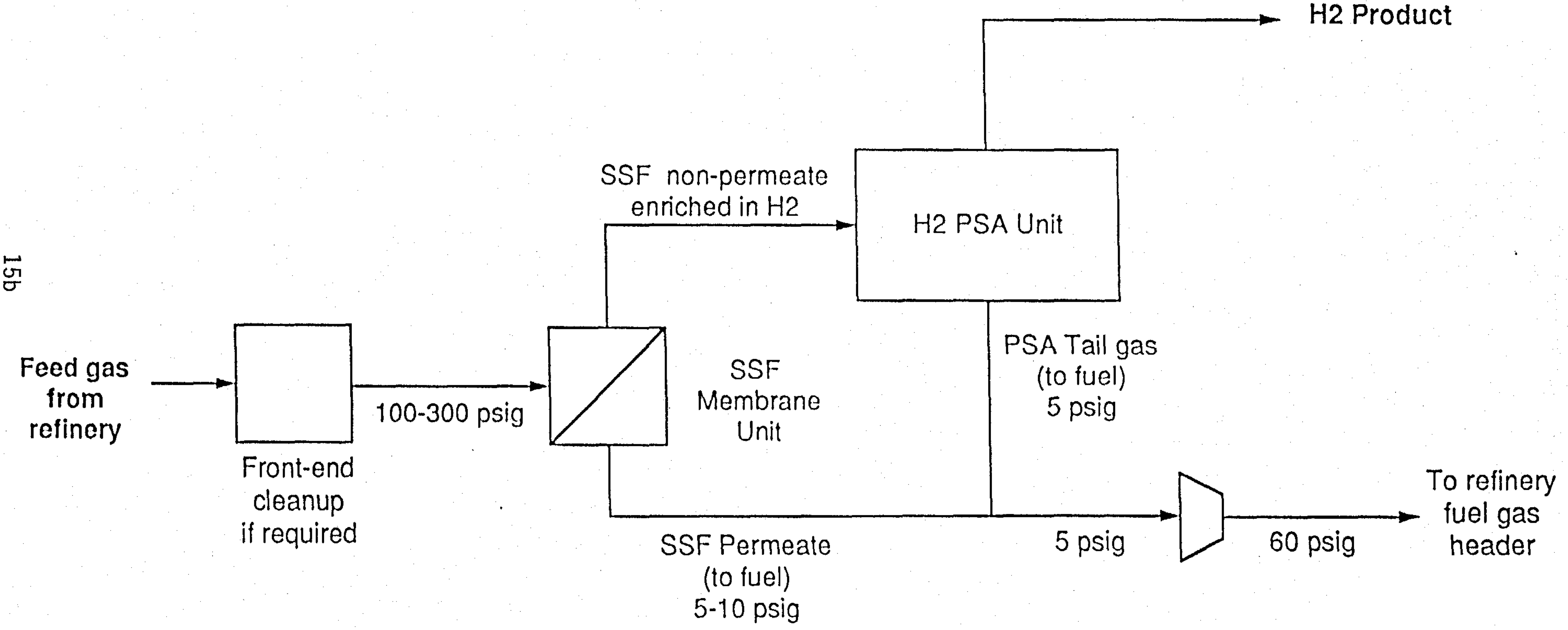
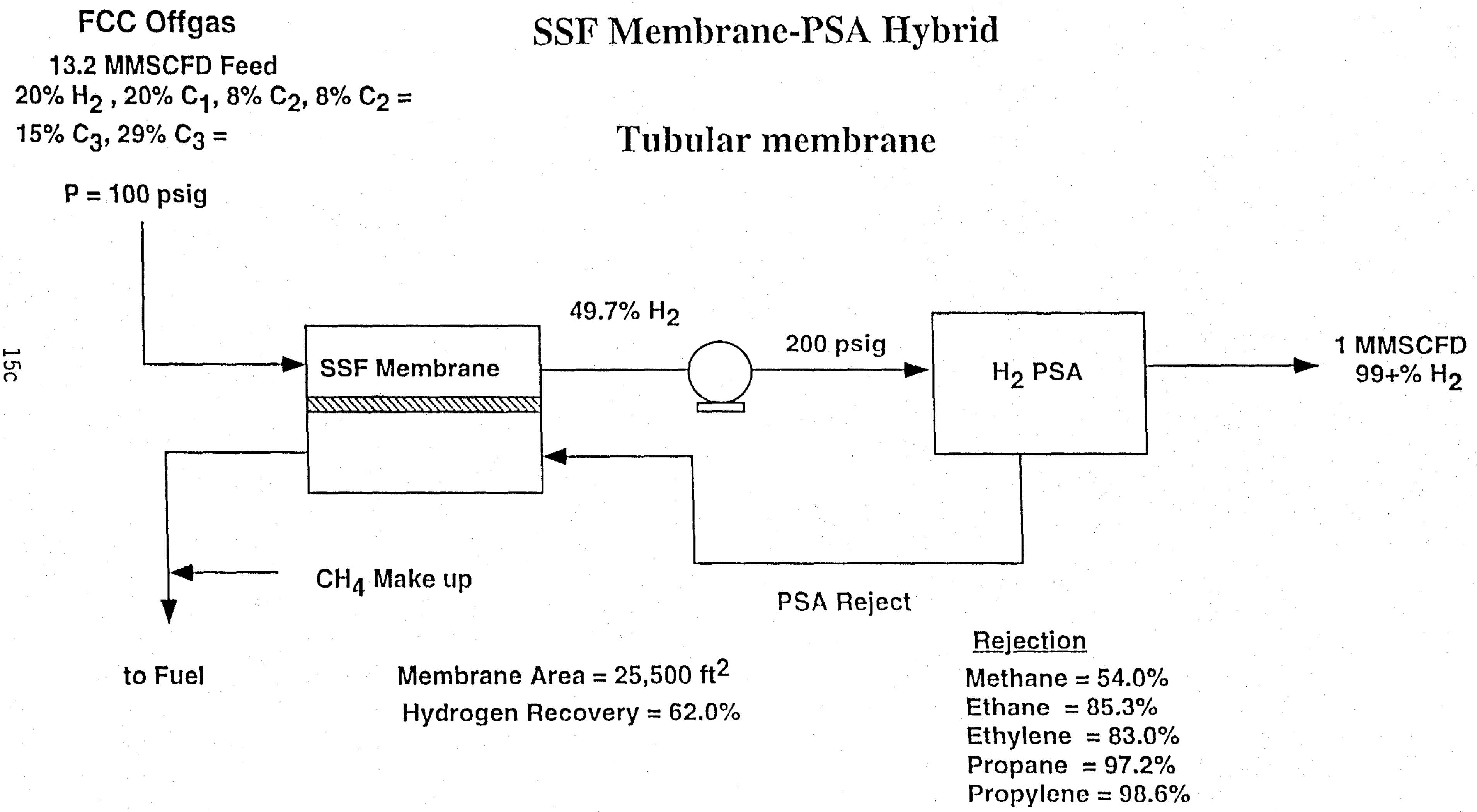


Figure 37. Process Flow Diagram for Recovery of H_2 from Refinery Off-Gas Stream

Hydrogen Recovery from Refinery Waste Gases

SSF Membrane-PSA Hybrid

Tubular membrane



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

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%

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

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 H_2 Recovery in H_2 Plants

Feed : H_2 (23-49%) $+CO_2+CH_4+CO$; 2-6 atm feed pressure

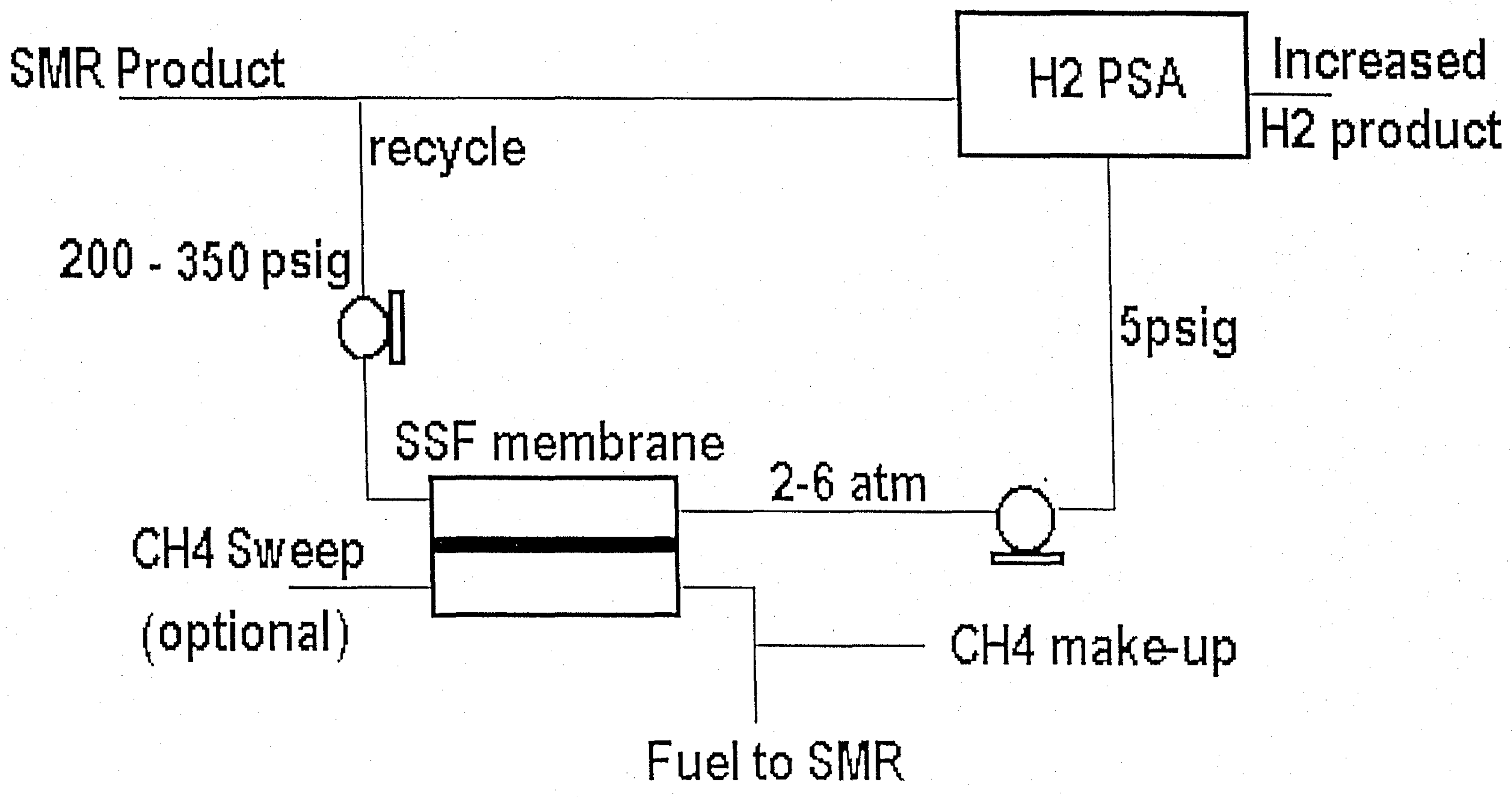


Figure 39. SSF-PSA Hybrid for Enhanced Hydrogen Recovery in H_2 Plants

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			
<u>Energy :</u>			
(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
<u>Waste :</u>			
<u>CO_2</u>	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
<u>NO_x</u>			
	10 lb/MM scf H_2	0	440 T/yr

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7.0 ACKNOWLEDGEMENTS

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APPENDIX I

Phase I Program Plan and Milestones

FORM EIA-459B
(10/80)

U.S. Department of Energy

FEDERAL ASSISTANCE MILESTONE PLAN

FORM APPR
OMB No. 190

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)

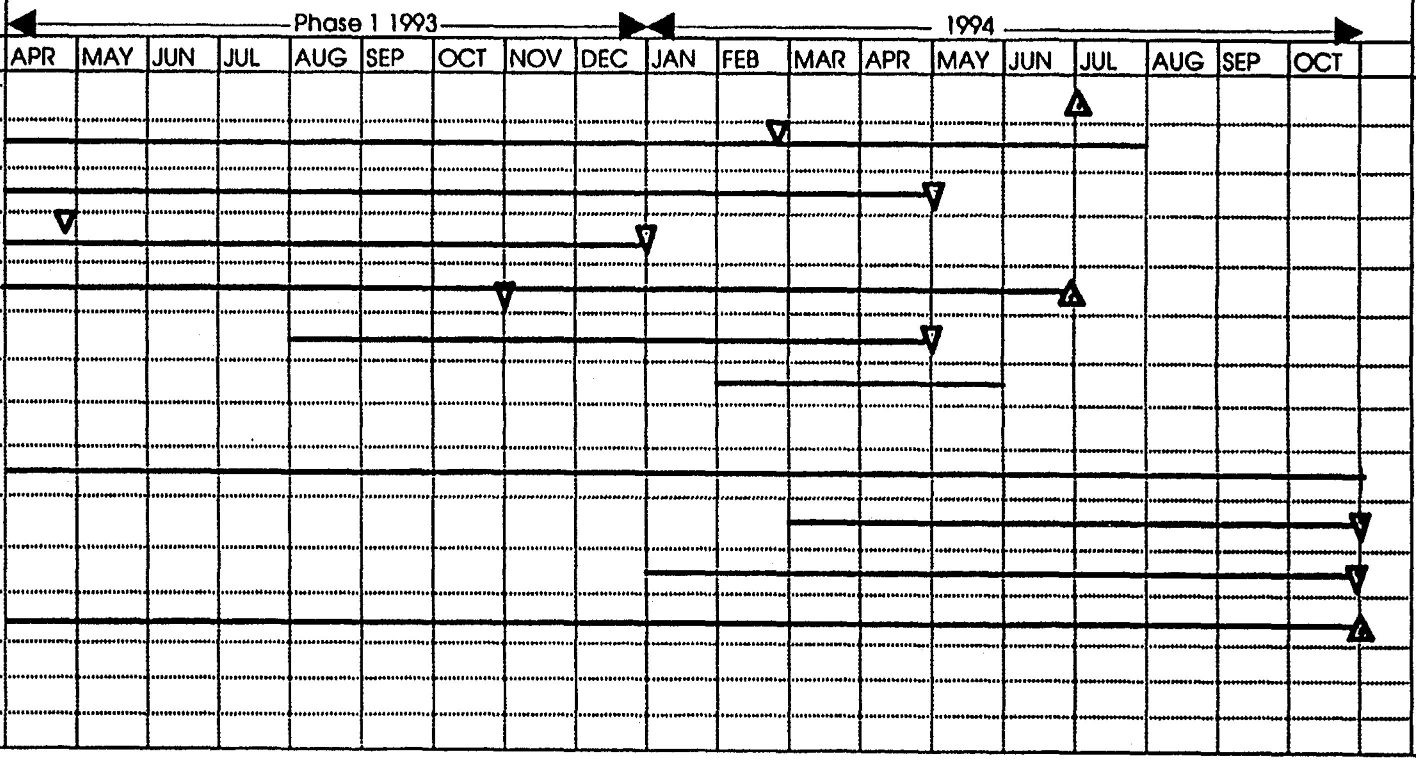
Air Products and Chemicals, Inc.
Corporate Science and Technology Center
7201 Hamilton Blvd.
Allentown, PA 18195-1501

4. Program/Project Start Date **April 1 1993**

5. Program/Project Completion Date **May 31 1997**

6. Identification Number	7. Planning Category (Work Breakdown Structure Tasks)
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/Contstruct 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

8. Program/ Project Duration



9. Comments (Notes, Name of Performer)

10. Remarks

11. Signature of Recipient and Date M-Anand Nov 23, 93

12. Signature of DOE Reviewing Representative and Date

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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