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

Phase II: Technology Development

Final Report

**By
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April 1996

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**For
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Office of Industrial Technologies
Washington, DC**

**By
Air Products and Chemicals, Inc.
Allentown, Pennsylvania**

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Prepared by
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PREFACE

This report documents Phase II, Technology Development, which was performed over the period November 1994 through October 1995. It is the second phase of a three phase project for the development of Selective Surface Flow (SSFTM) membranes for the recovery of hydrogen from off-gas streams from various chemical/refinery operations.

In Phase I of the work, the basic laboratory scale technology was developed. In addition, the membrane architecture and the separations device were defined. 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 second phase focused on (i) engineering data development, (ii) field testing of the membrane, (iii) technology transfer to manufacturing stage and demonstration of manufacturability and (iv) design and economic analysis with increased detail and rigor.

Engineering data were developed for two applications : (a) H₂ recovery from waste gas mixtures of H₂ and light hydrocarbons (C1-C4's) and (b) increased H₂ production in plants producing H₂ by steam methane reforming (SMR) followed by purification in a H₂ pressure swing adsorption (PSA) system. The membrane performance data was generated over a wide range of gas compositions and feed pressures. A membrane test unit with 1 ft² membrane area was installed at the APCI hydrogen plant in Martinez, CA for field testing. The following were concluded from the field test : (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. SSF membrane preparation was scaled up at Golden Technologies Company (GTC), Golden, Co. With improved preparation methods, an SSF membrane with improved separation properties was demonstrated at GTC. Detailed economic analysis showed that the technology is attractive for hydrogen recovery from refinery waste streams. An energy reduction of 13% is estimated for H₂ recovery via this process which results in significant reductions in NO_x and CO₂ emissions.

In Phase III, the technology will be demonstrated by scaling 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 and Keith Ludwig were the Program Managers for Phase II of the program. The principal investigators were M. Anand, K. Ludwig, T. Naheiri and J. Yang. Barry Halper is the Contracting Manager. Additional technical contributors to the program were Beth Campion-Louie, Sheila Wirth, Randy Weber and Keith Fabregas. Shivaji Sircar and Madhukar Rao have been active consultants in this work.

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1.0 EXECUTIVE SUMMARY

Selective Surface Flow (SSFTM) membranes are a novel class of gas separation membranes developed by Air Products and Chemicals Inc. (APCI) that represent a significant departure in membrane performance characteristics versus conventional polymer membranes. The membrane separates by selective adsorption on the membrane pore surface and selective surface diffusion through the membrane pores. While numerous applications have been identified for this membrane including hydrocarbon fractionation, H₂S/H₂ separations and drying of gas streams, the focus of this development program is on the separation of H₂ from hydrocarbons from refinery waste gas streams. Although the initial focus is on the recovery of hydrogen, valuable hydrocarbons can also be recovered from these streams. A significant attribute of the SSF separation process is that it allows H₂ to be recovered at its feed pressure so compressing the H₂ to its application pressure is reduced or avoided. The hydrocarbons are recovered at permeate pressure, which is typically close to atmospheric.

The basic laboratory scale technology for the membrane was developed in the first phase of the program [1]. The second phase focused on (i) engineering data development, (ii) field testing of the membrane, (iii) technology transfer to manufacturing stage and demonstration of manufacturability and (iv) design and economic analysis with increased detail and rigor.

Design data was generated for two applications: (i) H₂/hydrocarbon (C1 to C4 hydrocarbons) separation and (ii) increased H₂ recovery in H₂ plants. Data has been gathered over a wide range of compositions and pressures that are encountered in these applications.

A field test with 19-tube, 1 ft² membrane area module was carried out at the APCI hydrogen plant at the TOSCO refinery in Martinez, CA. A fuel gas imported from the TOSCO refinery, containing ~20% H₂ with hydrocarbons (~10% C₃'s) was fed to the membrane after pre-cleaning in a temperature swing adsorption (TSA) system to remove water and large hydrocarbon molecules (C₆+) from the feed to the membrane. A product stream containing 35-40% H₂ and <1% C₃'s was recovered as the high pressure effluent. Effects of varying feed compositions on membrane operation were investigated and a method was developed whereby an effluent with relatively constant product composition is obtained. The field test with the first module was carried out for 2 months over which no change in membrane performance was observed. Also, the field data closely matched the lab data. The field test was considered very successful. The field test is now continuing with 3.5 ft long tubular membranes produced in the manufacturing environment.

Technology for membrane preparation was transferred to Golden Technologies Company, (GTC) Golden, CO who will be jointly preparing the semi-commercial unit with APCI. The membrane was successfully scaled up from 1 ft long tubes to 3.5 ft long tubes. By improving the membrane preparation process, SSF membranes with significantly improved performance have been prepared at GTC. The improvement will lead to higher (~15%) recovery of H₂ while maintaining the hydrocarbon rejection through the membrane. This should reduce the cost of H₂ recovery via this route and make the technology even more attractive.

Process design with increased detail was carried out for a "typical" fluid catalytic cracker (FCC) waste gas stream identified from a study undertaken with Wright Killen Associates. The H₂ production cost is about 66% of conventional steam methane reforming with the SSF membrane even after adding more process equipment (i.e. front end clean-up and recompression of

permeate to fuel header pressure). The projections for energy savings show a substantial increase from the values reported in Phase I primarily due to an increase in the estimated market size. The waste reduction estimate has not changed significantly.

2.0 SELECTIVE SURFACE FLOW MEMBRANES

2.1 Objectives:

The objective of Phase II of the Selective Surface Flow Membrane program was Technology Development. The key issues to be addressed were: (i) to develop detailed performance characteristics on a 1 ft² multi-tube module and develop design data, (ii) to build a field test rig and complete field evaluation with the 1 ft² area membrane system, (iii) to implement membrane preparation technology at partner site and demonstrate membrane performance in 3.5 ft long tube, (iv) to complete detailed process design and economic analysis.

2.2 Background/Summary of Phase I Work:

Selective Surface Flow (SSFTM) is a novel carbon membrane developed by Air Products and Chemicals Inc. This membrane separates by selective adsorption and surface diffusion through the membrane pores. This mechanism imparts separation properties not achievable in conventional glassy polymer 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 H₂ stream using a H₂ pressure swing adsorption (PSA) purification system. The SSF membrane concept was demonstrated on flat supports 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 2-3 micron 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 was achieved in Phase I of the program:

- (i) A low cost alumina support was developed for supporting the thin membrane coating.
- (ii) A reproducible coating process was developed for SSF membrane preparation.
- (iii) Tubular membrane separation and permeability properties were exceeded vs the benchmark with sheet membranes, and those 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 ft² membrane area.
- (v) A multi-tube module (19 tubes, 1 ft long) with 1 ft² 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 were 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 studied and temperature coefficients for H₂ recovery and propylene rejections were calculated.
- (x) First pass process design for recovery of H₂ 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 CO₂ and NO_x emissions are projected.

At the end of Phase I, the key technical objectives in the scale-up of SSF membranes were met and the project was ready for field testing and technology transfer to manufacturing. In Phase I, all targets were exceeded, and the work was completed on time.

2.3 Phase II Project Plan:

The project plan and milestones for Phase II of the program are shown in Appendix I. The key milestones were:

- (a) Obtain design data on multi-tube module.
- (b) Build field test unit and complete field evaluation.
- (c) Demonstrate membrane on 3.5 ft long tubes at partner facility and have membrane fabrication process in place.
- (d) Complete detailed process design and economic analysis.

Work carried out to meet these milestones is described in detail in the following sections.

3.0 TECHNOLOGY DEVELOPMENT

3.1 Design Data on SSF Membrane:

One of the applications of the SSF membrane is in the recovery of H₂ from refinery waste gas streams. The waste gas is fed to the membrane on the bore side and a H₂-enriched

stream is recovered as the high pressure effluent. The permeate stream is enriched in the higher hydrocarbons. Figure 1 shows the generic process scheme for recovering H_2 from such streams. As an initial target, a typical waste stream from a refinery fluid catalytic cracker (FCC) was selected for most lab characterizations. However, the composition and pressure of the waste streams can vary significantly from one refinery to another. The feed may typically contain H_2 and C_1 's to C_4 's and the feed pressure can vary from 100 to 300 psig. Thus, it was deemed necessary to develop a database representing a wide range of feed compositions and to determine the effects of composition and pressure variations on the membrane performance. In addition, this data would be used for developing a mathematical model which can be used to predict the membrane performance with an untested composition. Table 1 summarizes the list of compositions tested on the multi-tube module as a part of the database.

Table 1
List of Compositions Evaluated for H_2 /Hydrocarbon Separations

Data gathered at 3 and 7 atm feed pressures

Composition	Volume % H_2	Volume % C_1	Volume % C_2	Volume % C_3	Volume % C_4
1.	20	20	16	44	0
2.	20	20	30	20	10
3.	20	40	20	10	10
4.	20	20	30	28	2
5.	50	40	5	3	2
6.	50	20	20	8	2
7.	20	40	20	18	2
8.	50	20	10	10	10
9.	43	34	17	6	0
10.	22	53	22	3	0

Figures 2 through 6 show typical recovery-rejection-A/F curves for several of the compositions. While the data is being used to develop a model, some of the important observations from the data are:

- (i) For all the compositions, high rejections (80-99%) for C_3 and C_4 species are obtained while recovering 50-70% H_2 .
- (ii) The membrane area required for separation (i.e. A/F) decreases as the feed pressure is increased.
- (iii) The membrane area required for separation increases with the rejection of hydrocarbons and with higher molecular weight hydrocarbons in the feed gas.
- (iv) The rejection of C_4 's increases at higher feed pressures for the compositions that contain low levels of C_4 's.

Figure 1
Process Flow Diagram for Base Case Application in Hydrogen Recovery

SSF Membrane - PSA Hybrid

C4 Rejection vs H2 Recovery with Varying Compositions; 3 atm

Figure 2

C3 Rejection vs H2 Recovery with Varying Compositions; 3 atm

Constituents, Vol % as listed in Table 1

Figure 3

C2Rejection vs H2 Recovery with Varying Compositions; 3 atm

Constituents, Vol % as listed in Table 1

Figure 4

C1 Rejection vs H2 Recovery with Varying Compositions; 3 atm

Constituents, Vol % as listed in Table 1

Figure 5

A/F vs H2 Recovery with Varying Compositions; 3 atm

Figure 6

- (v) The rejection of individual hydrocarbons is a complex interplay of the composition and pressure and generalizations can be misleading. The effects will be incorporated into the model being developed.

A second application of the SSF membrane being developed is the recovery of H_2 from H_2 -PSA waste streams in H_2 production. In this case, the waste gas is a mixture of H_2 , CO_2 , CO and CH_4 . The SSF membrane is integrated with the PSA to increase the total H_2 recovered in the plant (Figure 7). Increase of 5-12% in H_2 production can be achieved by this integration. A large amount of data was collected for this process scheme over a range of ($H_2+CO_2+CH_4$) compositions and pressures (note : CO was replaced by CH_4 in lab tests). The range of compositions reflects the fact that the H_2 recovery in the PSA can vary from 75% to 90% depending on the PSA design, operation conditions and the H_2 purity desired. Figures 8-10 show the data generated. This data can be used to design and optimize such a scheme. This data is also being incorporated into the performance model being developed for the membrane.

3.2 Field Test of SSF Membrane:

The objectives for testing the membrane in the field were:

- (a) determine the robustness of the membrane in a real feed stream as opposed to the simulated streams used in the laboratory,
- (b) determine the effect of feed variations (composition, temperature) on the membrane performance,
- (c) develop a membrane operation method to overcome feed variations,
- (d) ensure the membrane has a shelf-life greater than the life of the field test
- (e) evaluate the effect of contaminants on the membrane performance.

The site selected for performing the field test was the APCI H_2 plant located at the TOSCO refinery in Martinez, CA. The feed is a fuel stream imported from the TOSCO refinery into the H_2 plant. The feed contains: 21% H_2 , 50% CH_4 , 5% C_2H_4 , 15% C_2H_6 , 4% C_3H_6 and 5% C_3H_8 and trace amounts of higher hydrocarbons, H_2S , nitrogen, oxygen and water vapor.

A membrane system was built which consists of (a) a pre-treatment system to remove the heavy hydrocarbons, H_2S and water (a temperature swing adsorption system), (b) 1 ft² multi-tube module membrane (1 ft long tubes), (c) an on-line GC system for analysis of the feed and effluent streams, (d) an automation system for system control and remote operation, (e) data base for data collection and analysis. The pretreatment system allows one to control the species allowed into the membrane. Thus, the pretreatment unit can be controlled to allow the entry of C_4 , C_5 or C_6 into the membrane. Most of the membrane operation was carried out by eliminating hydrocarbons $>C_3$'s. Figure 11 shows a photograph of the SSF membrane skid in the field and Figure 12 shows a cut-out from the multi-tube module.

Figure 7
SSF-PSA Hybrid for Enhanced H₂ Recovery in H₂ Plants

Figure 8

Process Design Data for Higher H₂ Recovery from H₂ Production by SMR- PSA : 90% H₂ Recovery in PSA

23% H₂ + 58% CO₂ + 18% CH₄ + 1% N₂

Figure 9
**Process Design Data for Higher H₂ Recovery from H₂ Production by SMR-
 PSA : 80% H₂ Recovery in PSA**

36% H₂ + 54% CO₂ + 10% CH₄

36% H₂ + 54% CO₂ + 10% CH₄

Figure 10
Process Design Data for Higher H₂ Recovery from H₂ Production by SMR-
PSA : 75% H₂ Recovery in PSA

Figure 11 : SSF Membrane Skid for Field Testing Showing Gas Pretreatment Columns, Membrane and Control Box

Figure 12 : Cut-out View of Tubes in 19-Tube Module for Field Test

The membrane was tested at a feed pressure of 60 psig and the membrane temperature was same as that of the ambient. Figures 13-15 shows the variations in the feed composition and temperature vs time. The effect of variation in the feed composition is that the permeation through the membrane will change with composition. For example, as the C₃ composition in the feed increases, the flux of less permeable species decreases at the same feed rate to the membrane and hence more H₂ is recovered in the high pressure effluent. However, as the H₂ recovery increases, the concentration of C₃ in the product stream increases. The overall system needs to be operated at a constant C₃ in the product stream so that the product stream being fed to the PSA for H₂ purification does not reduce the H₂ recovery in the PSA (higher C₃ will reduce H₂ recovery in the PSA). This problem was overcome by operating the membrane at a constant (high pressure effluent flow rate)/(feed flow rate) ratio. In addition, this ratio allows one to operate at different H₂ recoveries. This is a simple and elegant process control strategy, the results from which are shown in Figure 16.

Figures 17 and 18 show the ethylene and propylene rejections at different hydrogen recoveries. Included in these Figures is data from the laboratory test with a simulated similar mixture. The data show that the membrane performance in the field is similar to that obtained in the lab. Figures 19 and 20 show propylene rejection and the membrane A/F vs H₂ recovery for continuous testing over a period of 2 months. The data show that the performance did not change over the 2 month test period. The scatter in the data is due to errors in flow and composition measurement, and temperature and composition fluctuations.

The test on this module was discontinued after 2 months. This module, with 1 ft long tubes, was replaced by a new module which was prepared with 3.5 ft long tubes. The results from the module with 3.5 ft long tubes are better than that from the previous module and will be detailed in the Phase III report.

In conclusion, the field test data with 1 ft long tubes shows that the SSF membrane can be used for recovering a H₂-enriched stream from a waste fuel stream with a front end pretreatment. The field performance data matches the laboratory measured data, and the membrane is stable after 2 months of continuous testing. A control strategy has been developed to operate the membrane at a constant H₂ recovery or a hydrocarbon rejection.

3.3 Membrane Fabrication at Partner Facility:

Golden Technologies Co., Golden, CO was selected as the partner for preparing the tubular membrane for the semi-commercial unit. GTC will prepare the alumina tubes, coat the membranes and assemble the tubes in a housing. The scaled-up membrane module will be a larger version of the current shell-and-tube type of system. The tubes will be 3.5 ft long and will be permanently sealed in place by potting in a polymer as opposed to the current gasket seals.

Figure 13

Component Mole Fractions in the High Pressure Feed
to the Field Unit: H₂/C₁

Figure 14

Figure 15

Figure 16

Figure 17

Figure 18

Ethylene Rejection vs. H₂ Recovery for Field and Laboratory Data

Figure 19

Propylene Rejection vs. H2 Recovery for Module IV Field Unit

AF vs. H2 Recovery for Module IV Field Unit

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.

3.4 Process Design, Economics and Waste Reduction:

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 C_2 '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

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

Figure 23

Performance of Improved SSF Membranes
 20% H₂, 20% CH₄, 16% C₂'s, 44% C₃'s; Ph=3.0 atm, P₁=1.05 atm

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

<u>Gas</u>	<u>Volume Fraction</u>
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 H₂ available in waste gas in the US
2. 40% of the gas is amenable to recovery using SSF/PSA
3. 56% of the contained H₂ is recovered
4. Volume of H₂ recovered ~400 MM scfd

Energy Basis for Comparison

1. Current technology: SMR/PSA
2. Energy to produce H₂ by SMR/PSA = 420 BTU/scf
3. Energy saving = 13% by SSF/PSA
4. Heating value of CH₄ = 1000 BTU/scf; H₂ = 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% H₂, 30% C₁, 24% C₂, 7% C₃**

Case	Capital	Energy	Total H₂ Product Cost
SSF/PSA	0.5	0.87*	0.66
SMR/PSA	1.0	1.00	1.00
*Includes CH₄ make-up to refinery fuel system			

Waste Basis for Comparison

1. H₂ combustion produces ~10 lb NO_x/1 MMscf H₂ by SMR/PSA
2. CO₂ production by oxidation of methane: 1 mole CO₂/mole CH₄

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) H₂ recovery from waste gas mixtures of H₂ and light hydrocarbons (C1-C4's) and (b) increased H₂ production in plants producing H₂ by steam methane reforming (SMR) followed by purification in a H₂ pressure swing adsorption (PSA) system. The data was generated with various feed gas mixtures at a wide range of pressures.
2. A 1 ft² 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 H₂ 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 H₂ recovery vs on-purpose H₂ production at a produc volume of ~ 5 MM scfd H₂.
5. Energy savings of 7.8 - 55.8 x 10¹² BTU/yr are estimated for H₂ recovery via the SSF-PSA route for year 2010. CO₂ 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 H₂ in year 2010

	<u>Current Technology</u>	<u>Proposed Technology</u>	<u>Annual Saving in 2010</u>
<u>Description:</u>			
<u>Energy:</u>			
i) w/ CH ₄ make-up	420 BTU/scf 79590 BTU/lb	365 BTU/scf 69170 BTU/lb	7.8 x 10 ¹² BTU
ii) w/o CH ₄ make-up		26 BTU/scf	55.8 x 10 ¹² BTU
<u>Waste</u>			
<u>CO₂:</u>	3.5 x 10 ⁶ T/yr		
i) w/ CH ₄ make-up		3.3 x 10 ⁶ T/yr	0.2 x 10 ⁶ T/yr
ii) w/o CH ₄ make-up		0.7 x 10 ⁶ T/yr	2.8 x 10 ⁶ T/yr
<u>NO_x:</u>			
	10 lb/MM scf H ₂		700 T/yr

5.0 REFERENCES

1. Anand, M, "Novel Selective Surface Flow (SSFTM) Membranes for the Recovery of H₂ from Waste Gas Streams" Phase I: Exploratory Development; Final Report to Department of Energy, August 1995.

6.0 ACKNOWLEDGEMENTS

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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 ft² multi-tube module
- Develop design method for scaling up membrane to larger area
- Determine optimum operating conditions for membrane for H₂ 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 ft²)
- Demonstrate membrane performance in above module
- Develop membrane QC procedures
- Prepare 1 ft² 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 H₂ 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 H₂ business area agreement in place

Task 2.4 Update Projections Develop Commercialization Plan

- Improve estimates of market potential
- Determine energy and waste reduction for opportunities
- 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)

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