1.0 EXECUTIVE SUMMARY

Selective Surface Flow (SSF^{TM}) 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, H_2S/H_2 separations and drying of gas streams, the focus of this development program is on the separation of H_2 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 H_2 to be recovered at its feed pressure so compressing the H_2 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) H_2/hydrocarbon (C1 to C4 hydrocarbons) separation and (ii) increased H_2 recovery in H_2 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 ft^2 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% H_2 with hydrocarbons (~10% C_3's) was fed to the membrane after pre-cleaning in a temperature swing adsorption (TSA) system to remove water and large hydrocarbon molecules (C_6+) from the feed to the membrane. A product stream containing 35-40% H_2 and <1% C_3'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 H_2 while maintaining the hydrocarbon rejection through the membrane. This should reduce the cost of H_2 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 H_2 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 ft^2 multi-tube module and develop design data, (ii) to build a field test rig and complete field evaluation with the 1 ft^2 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 (SSF™) 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 H_2 stream using a H_2 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 ft^2 membrane area.
(v) A multi-tube module (19 tubes, 1 ft long) 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 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 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 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 H_2 from refinery waste gas streams. The waste gas is fed to the membrane on the bore side and a H_2-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

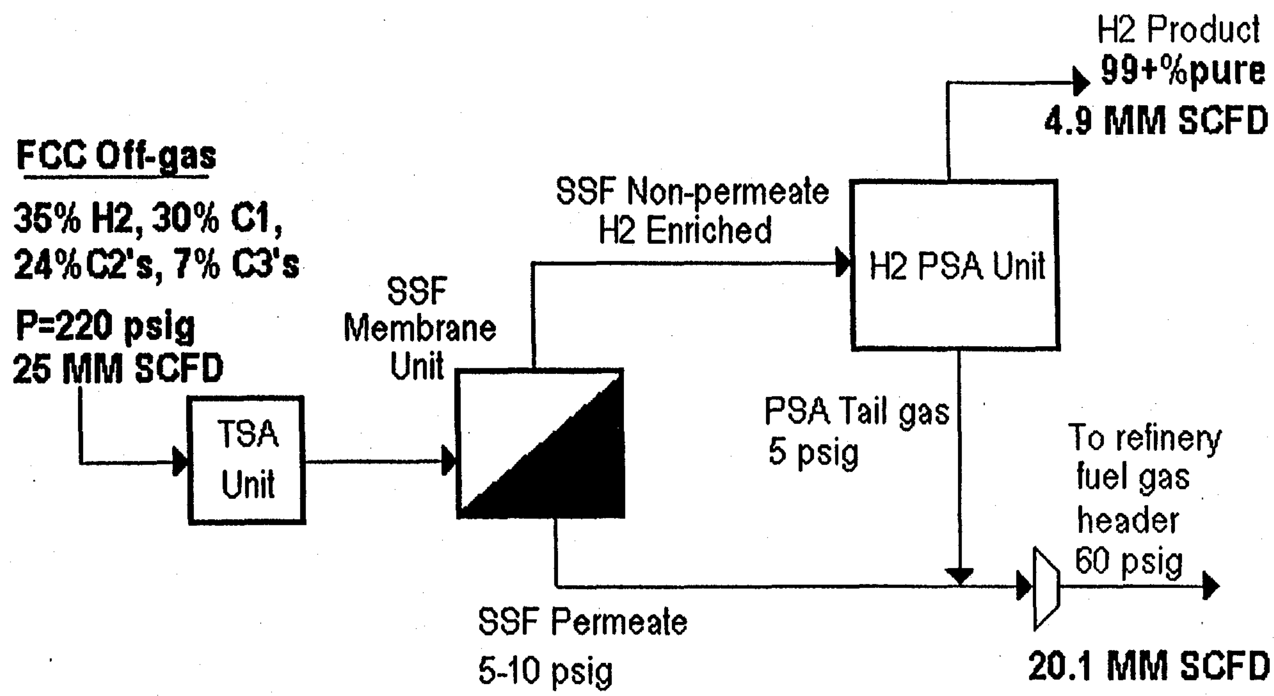
Composition	Volume % H_2	Volume % C1	Volume % C2	Volume % C3	Volume % C4
1.	20	20	16	44	0
2.	20	20	30	20	10
3.	20	40	20	10	10
4.	20	20	30	28	2
5.	50	40	5	3	2
6.	50	20	20	8	2
7.	20	40	20	18	2
8.	50	20	10	10	10
9.	43	34	17	6	0
10.	22	53	22	3	0

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



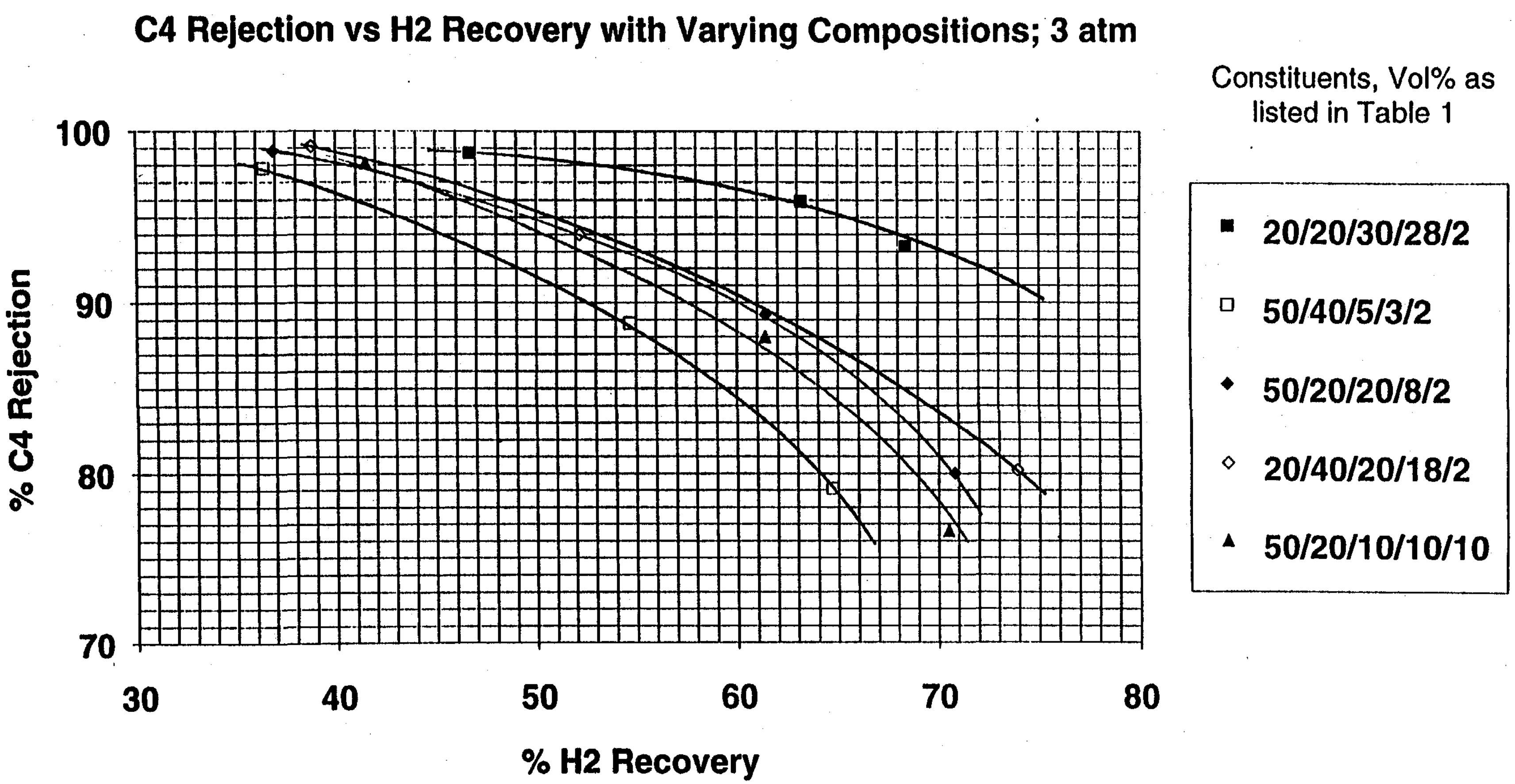

C4 Rejection vs H2 Recovery with Varying Compositions; 3 atm
Constituents, Vol% as listed in Table 1
20/20/30/28/2
50/40/5/3/2
50/20/20/8/2
20/40/20/18/2
50/20/10/10/10
100
90
80
70
% C4 Rejection
30
40
50
60
70
80
% H2 Recovery

Figure 2

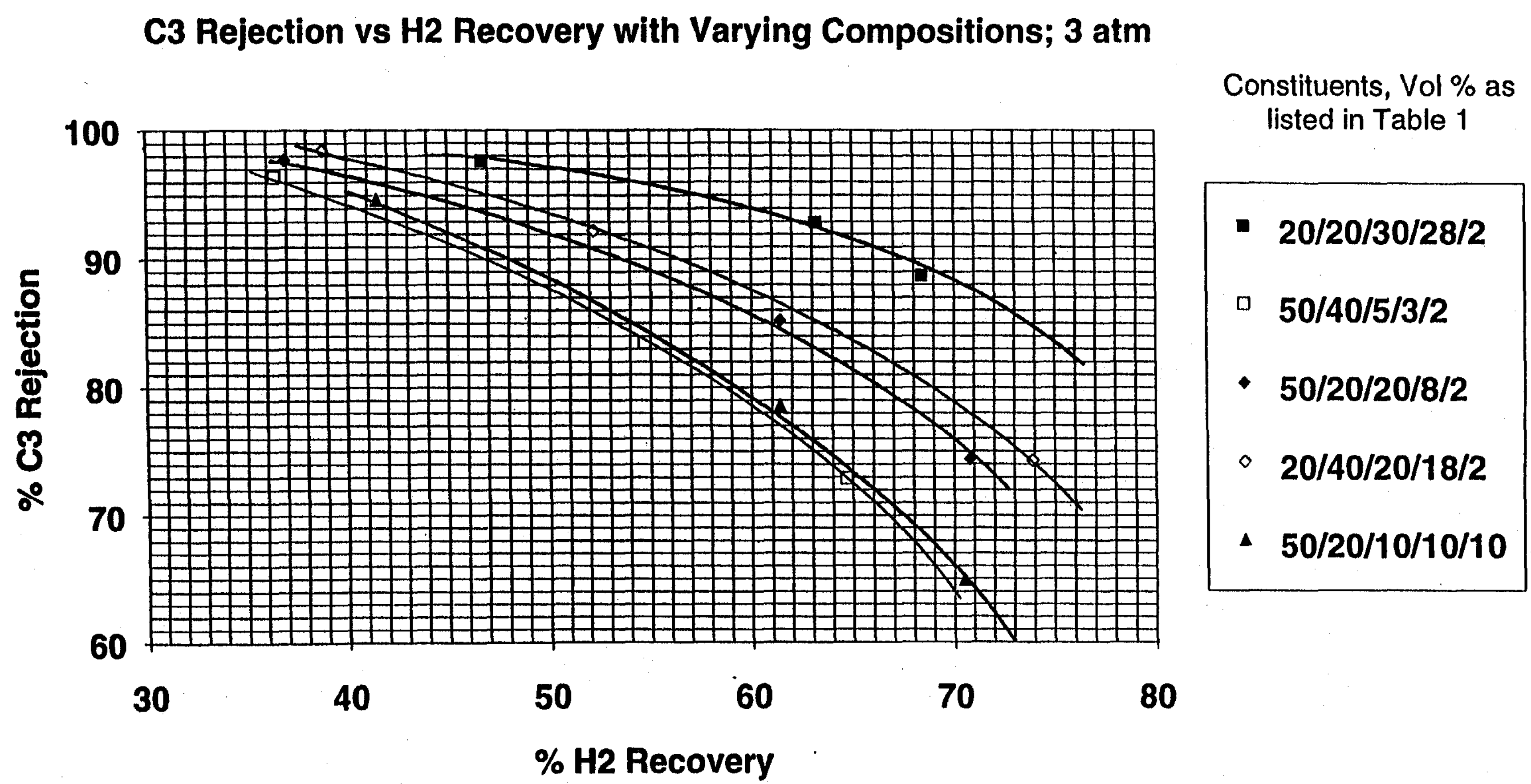

C3 Rejection vs H2 Recovery with Varying Compositions; 3 atm
% C3 Rejection
100
90
80
70
60
30
40
50
60
70
80
% H2 Recovery
Constituents, Vol % as listed in Table 1
20/20/30/28/2
50/40/5/3/2
50/20/20/8/2
20/40/20/18/2
50/20/10/10/10

Figure 3

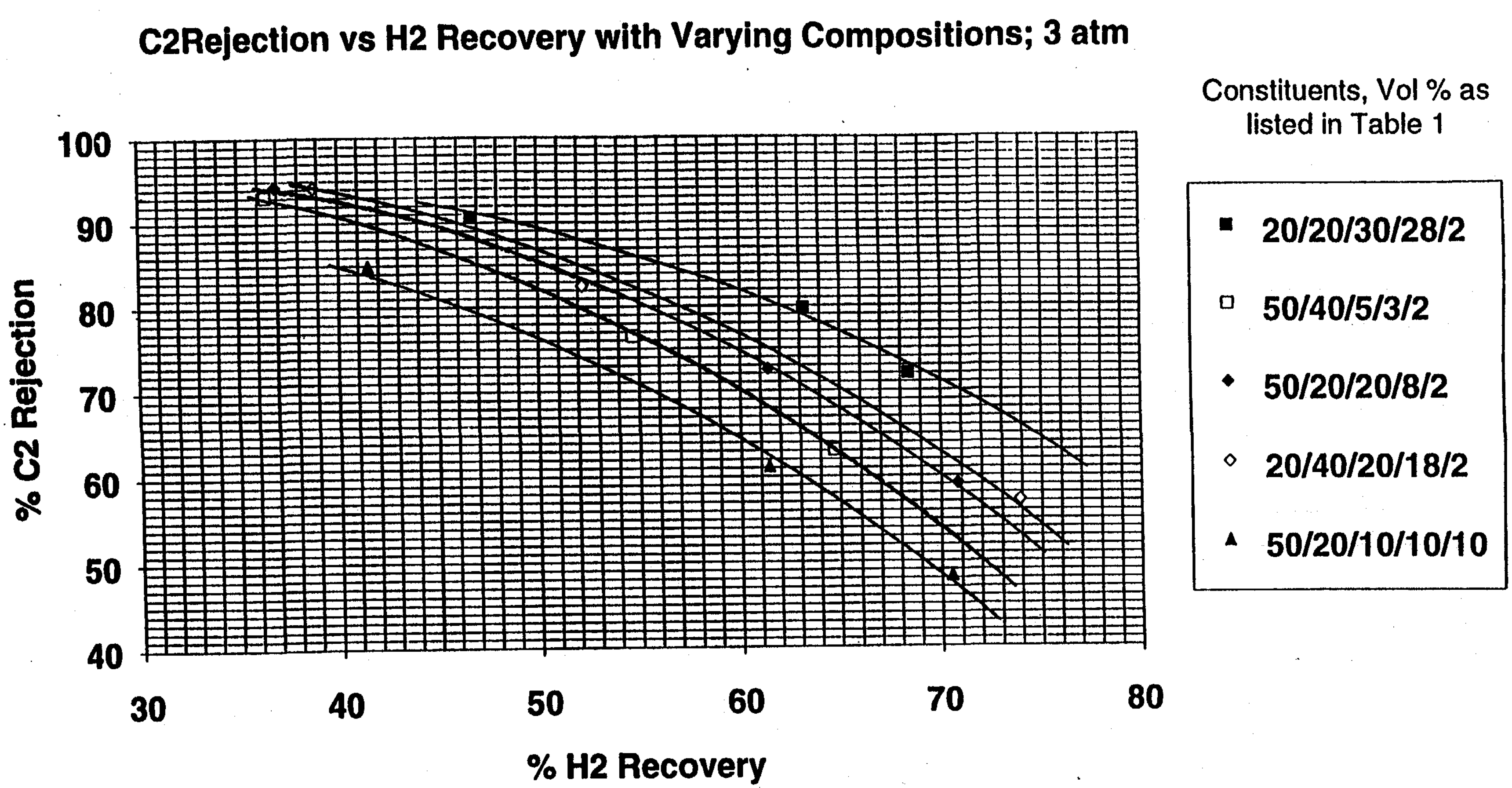

C2Rejection vs H2 Recovery with Varying Compositions; 3 atm
% C2 Rejection
100
90
80
70
60
50
40
30
40
50
60
70
80
% H2 Recovery
Constituents, Vol % as listed in Table 1
20/20/30/28/2
50/40/5/3/2
50/20/20/8/2
20/40/20/18/2
50/20/10/10/10

Figure 4

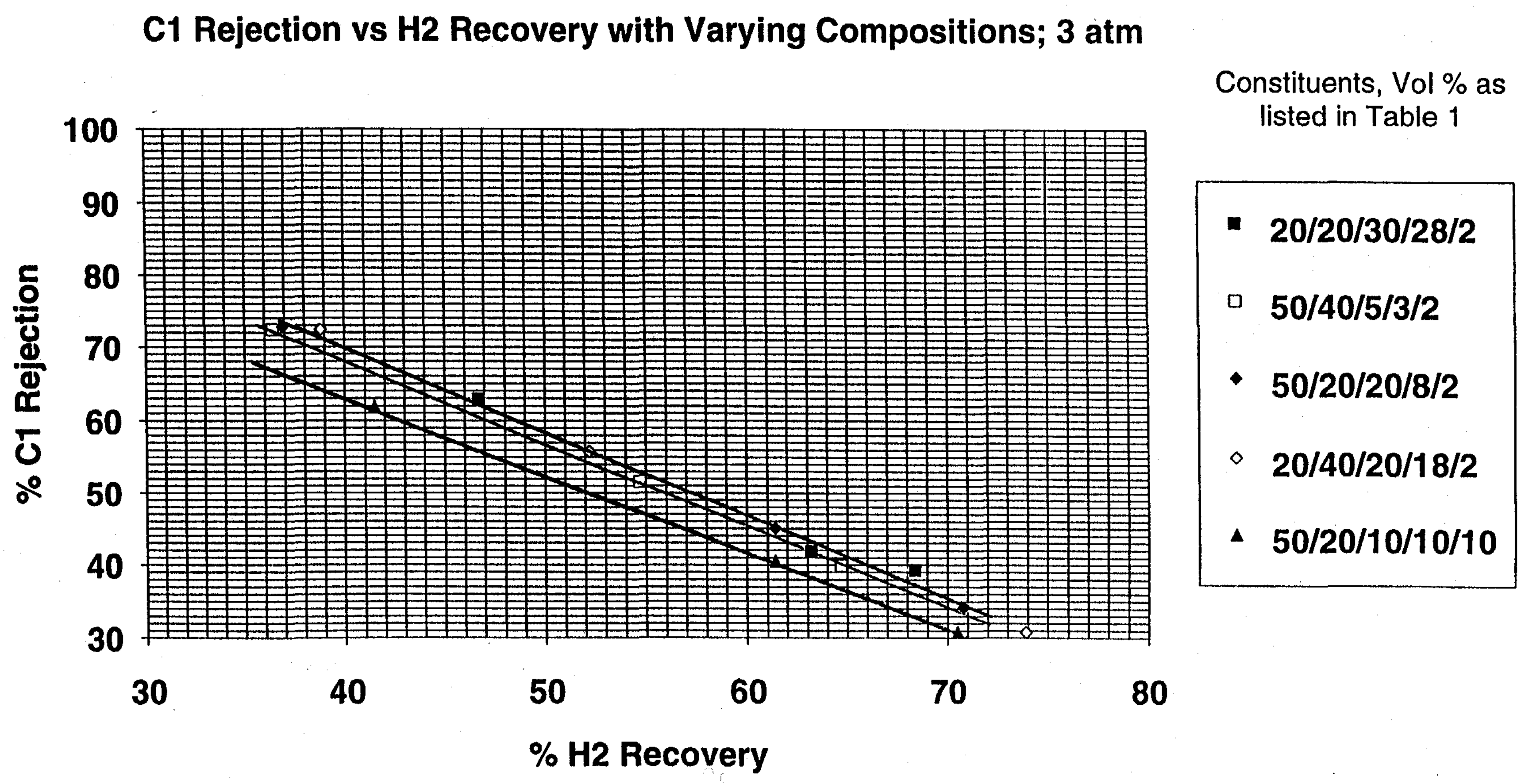

C1 Rejection vs H2 Recovery with Varying Compositions; 3 atm
% C1 Rejection
100
90
80
70
60
50
40
30
30
40
50
60
70
80
% H2 Recovery
Constituents, Vol % as listed in Table 1
20/20/30/28/2
50/40/5/3/2
50/20/20/8/2
20/40/20/18/2
50/20/10/10/10

Figure 5

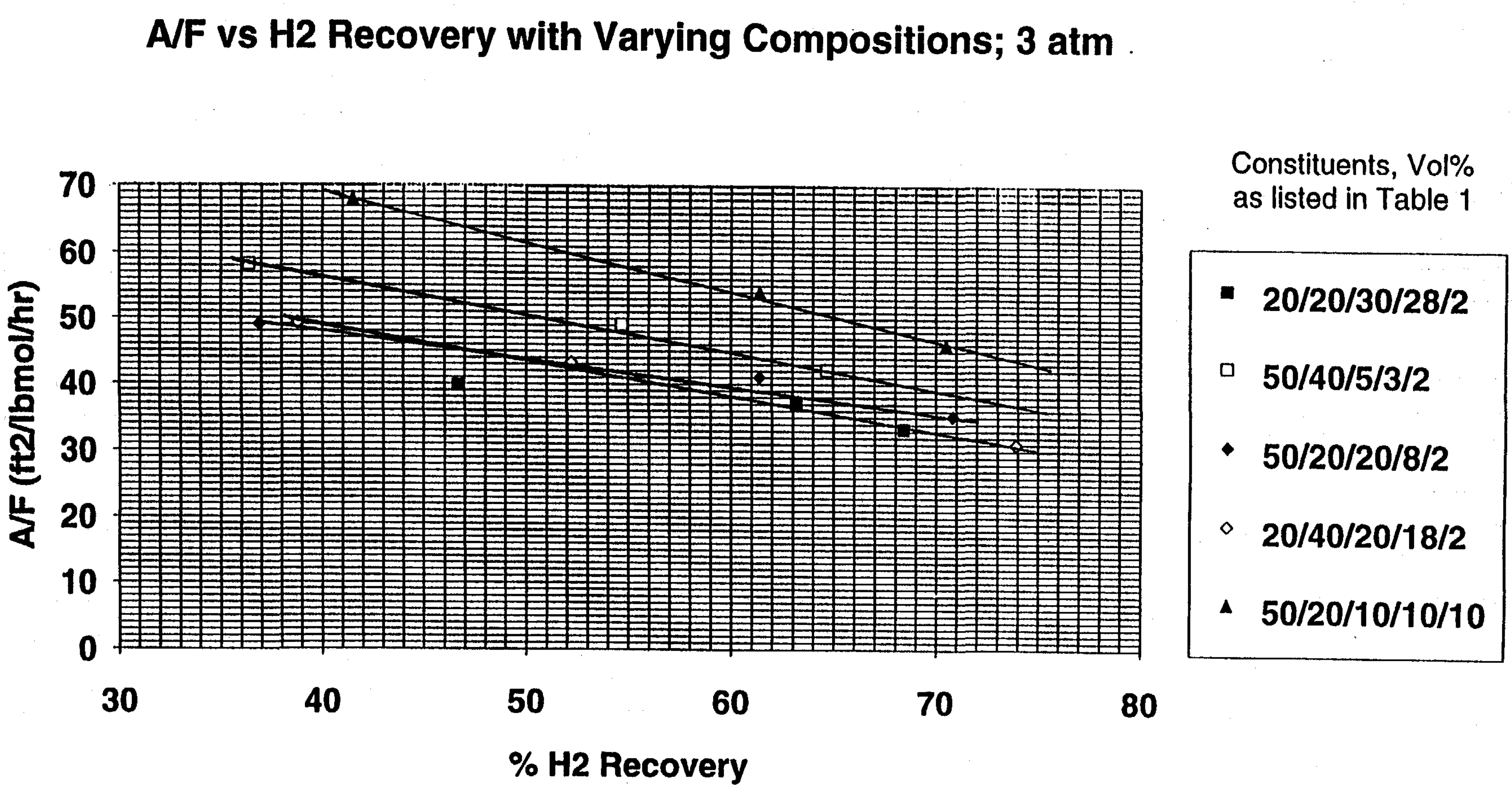

A/F vs H2 Recovery with Varying Compositions; 3 atm
A/F (ft2/lbmol/hr)
70
60
50
40
30
20
10
0
30
40
50
60
70
80
% H2 Recovery
Constituents, Vol%
as listed in Table 1
20/20/30/28/2
50/40/5/3/2
50/20/20/8/2
20/40/20/18/2
50/20/10/10/10

Figure 6