(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:

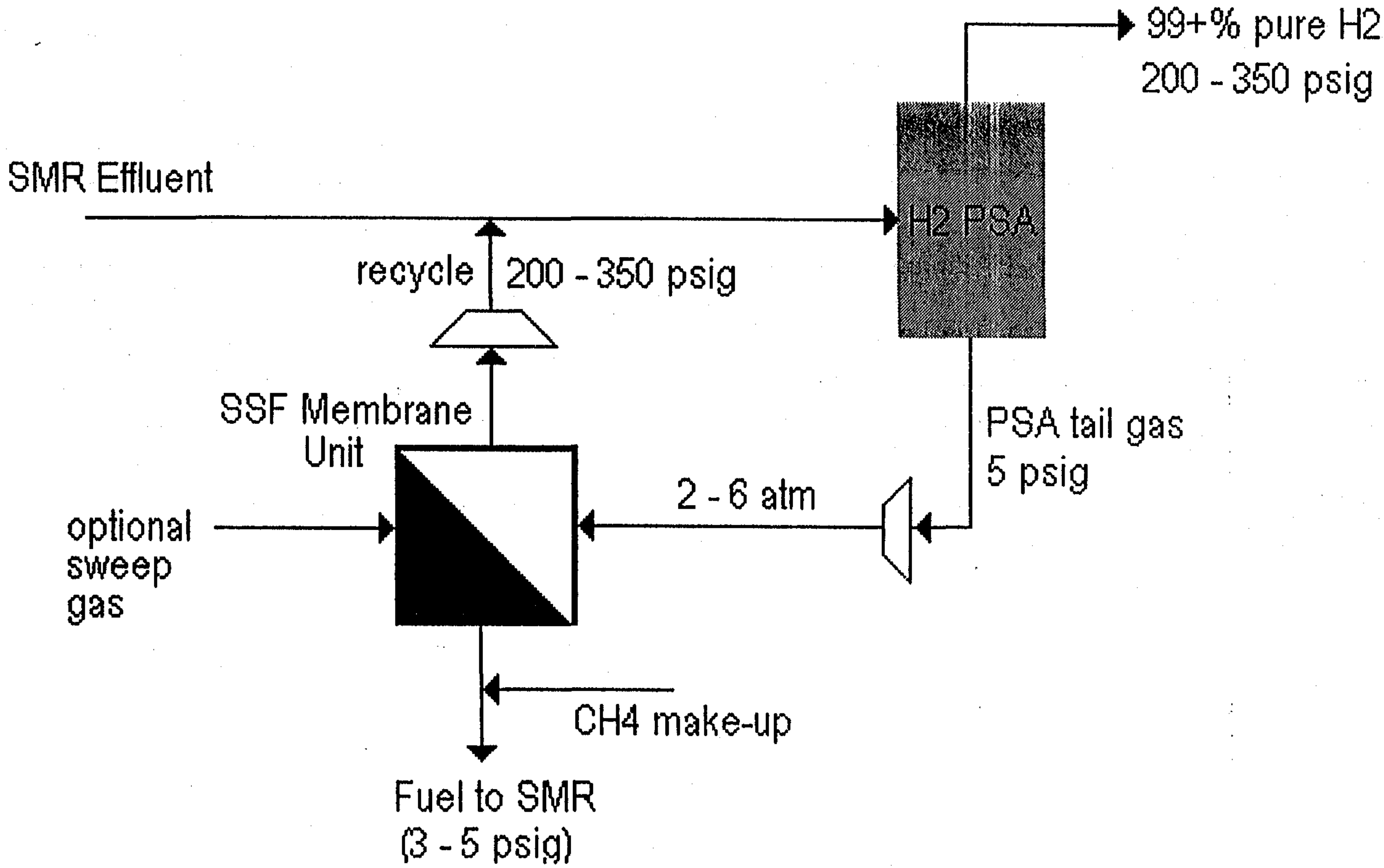
The objectives for testing the membrane in the field were:
(a) determine the robustness of the membrane in a real feed stream as opposed to the simulated streams used in the laboratory,
(b) determine the effect of feed variations (composition, temperature) on the membrane performance,
(c) develop a membrane 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 ft^2 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 H_2 Recovery in H_2 Plants

Feed : H_2 (23-49%), CO_2, CH_4, CO; 2-6 atm



c:phaseii1.doc

Figure 8
Process Design Data for Higher H_2 Recovery from H_2 Production by SMR-PSA : 90% H_2 Recovery in PSA

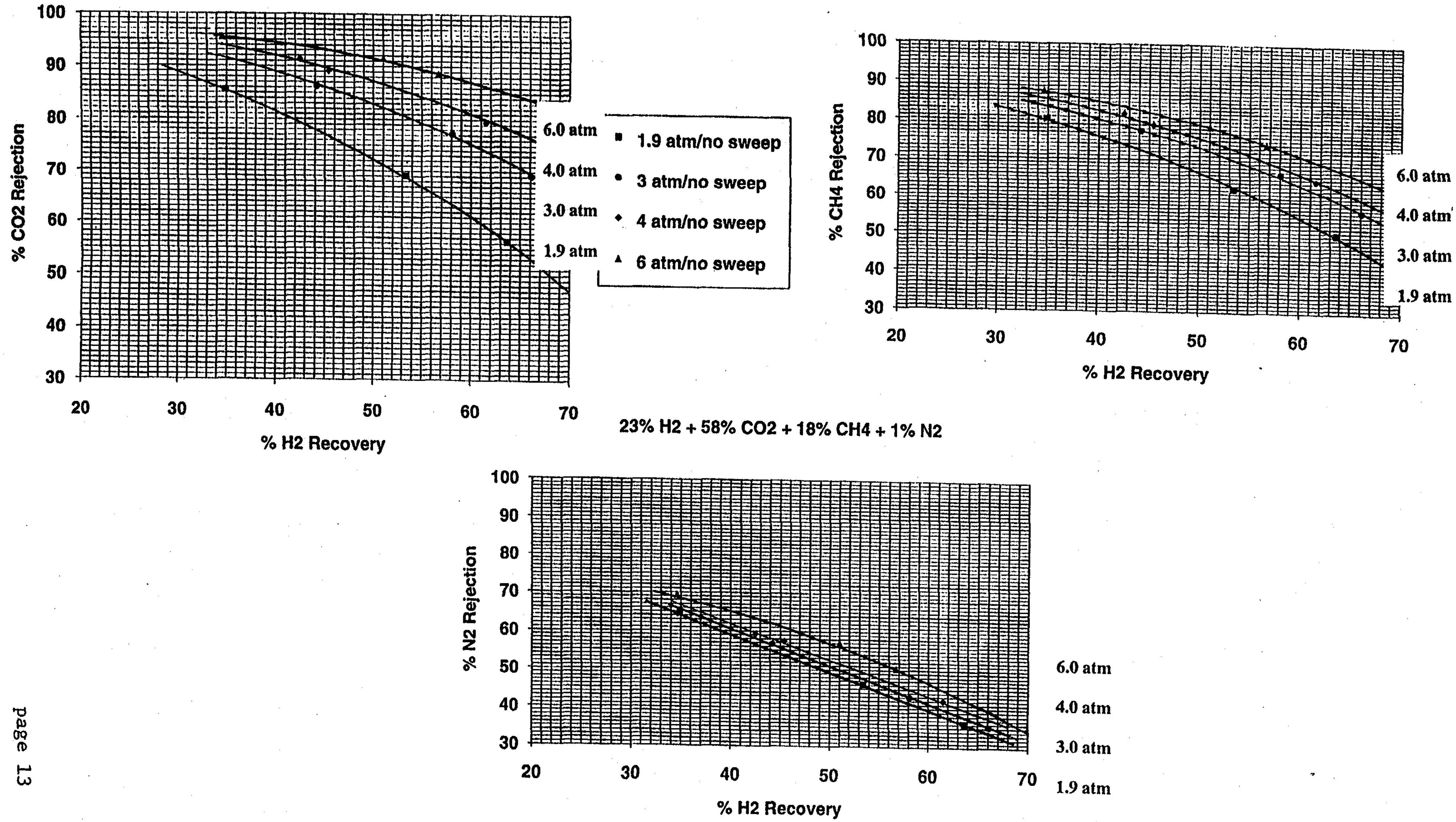


Figure 9
Process Design Data for Higher H_2 Recovery from H_2 Production by SMR-PSA : 80% H_2 Recovery in PSA

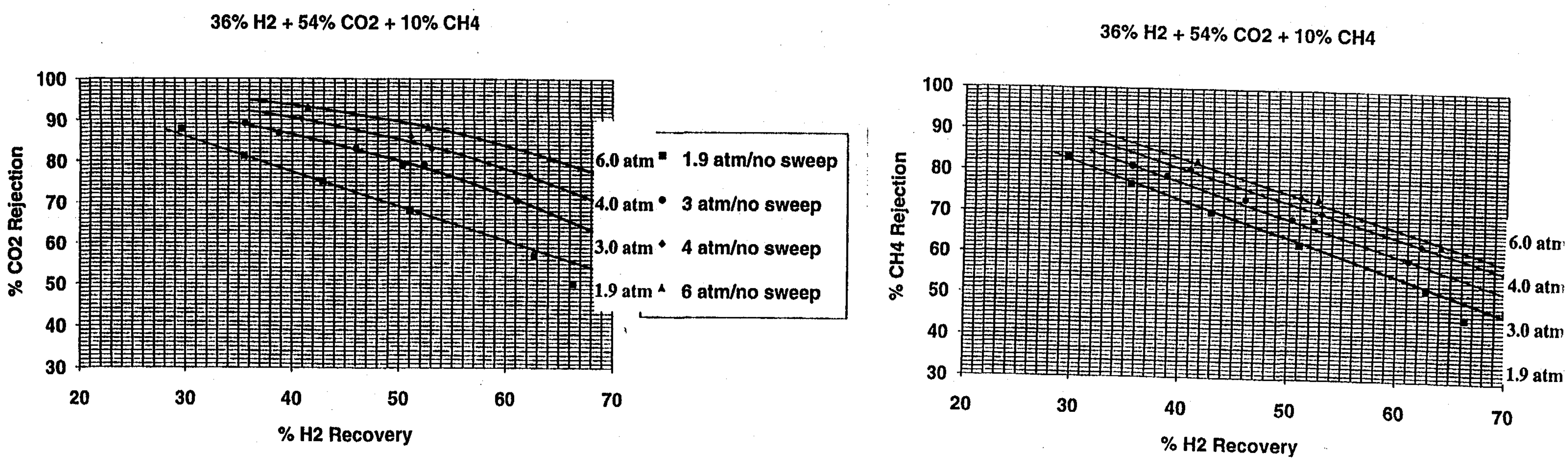
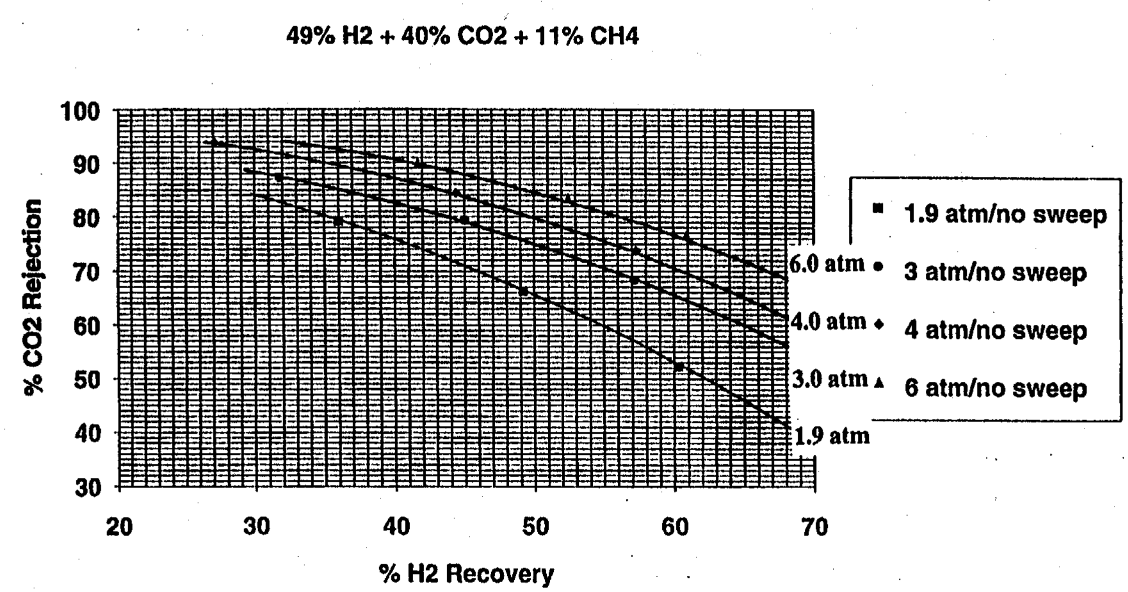


Figure 10
Process Design Data for Higher H_2 Recovery from H_2 Production by SMR-PSA : 75% H_2 Recovery in PSA



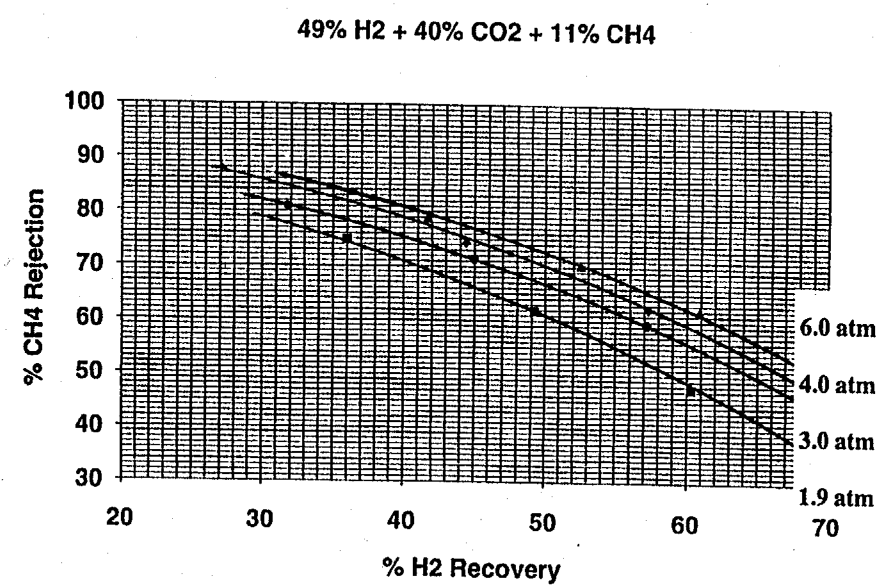


Figure 11 : SSF Membrane Skid for Field Testing Showing Gas Pretreatment Columns, Membrane and Control Box

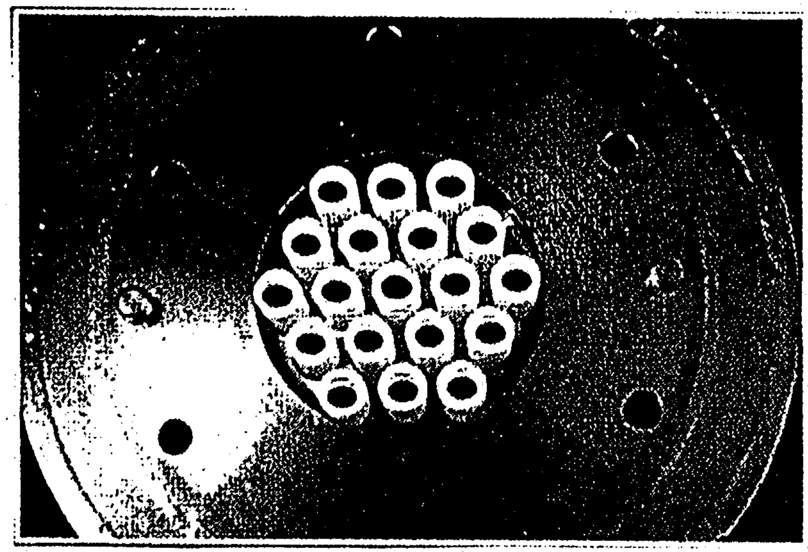


Figure 12 : Cut-out View of Tubes in 19-Tube Module for Field Test

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 C_3 composition in the feed increases, the flux of less permeable species decreases at the same feed rate to the membrane and hence more H_2 is recovered in the high pressure effluent. However, as the H_2 recovery increases, the concentration of C_3 in the product stream increases. The overall system needs to be operated at a constant C_3 in the product stream so that the product stream being fed to the PSA for H_2 purification does not reduce the H_2 recovery in the PSA (higher C_3 will reduce H_2 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 H_2 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 H_2 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 H_2-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 H_2 recovery or a hydrocarbon rejection.

<u>3.3 Membrane Fabrication at Partner Facility:</u>

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

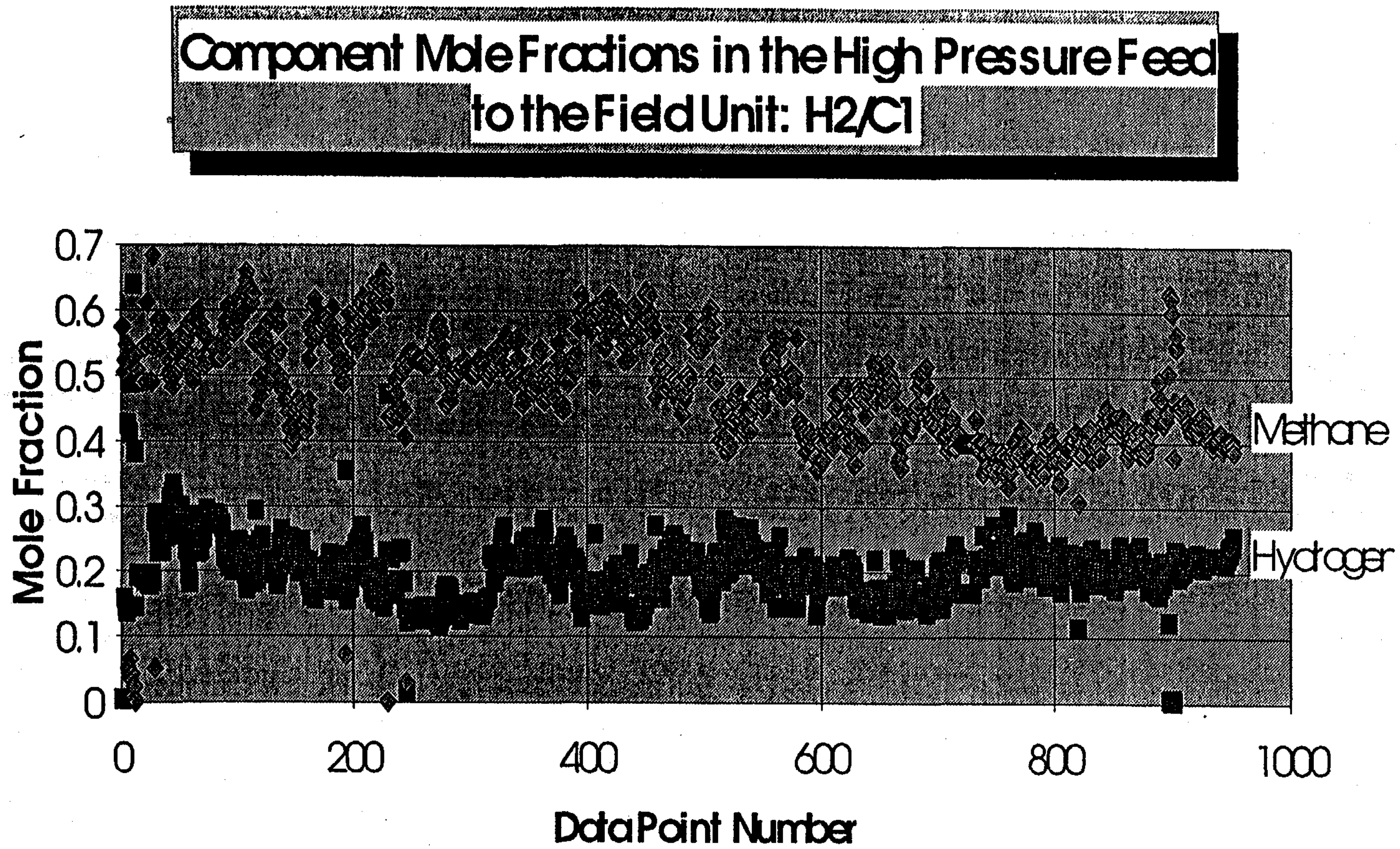

Component Mole Fractions in the High Pressure Feed to the Field Unit: H2/C1
Mole Fraction
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
Data Point Number
Methane
Hydrogen

Figure 14

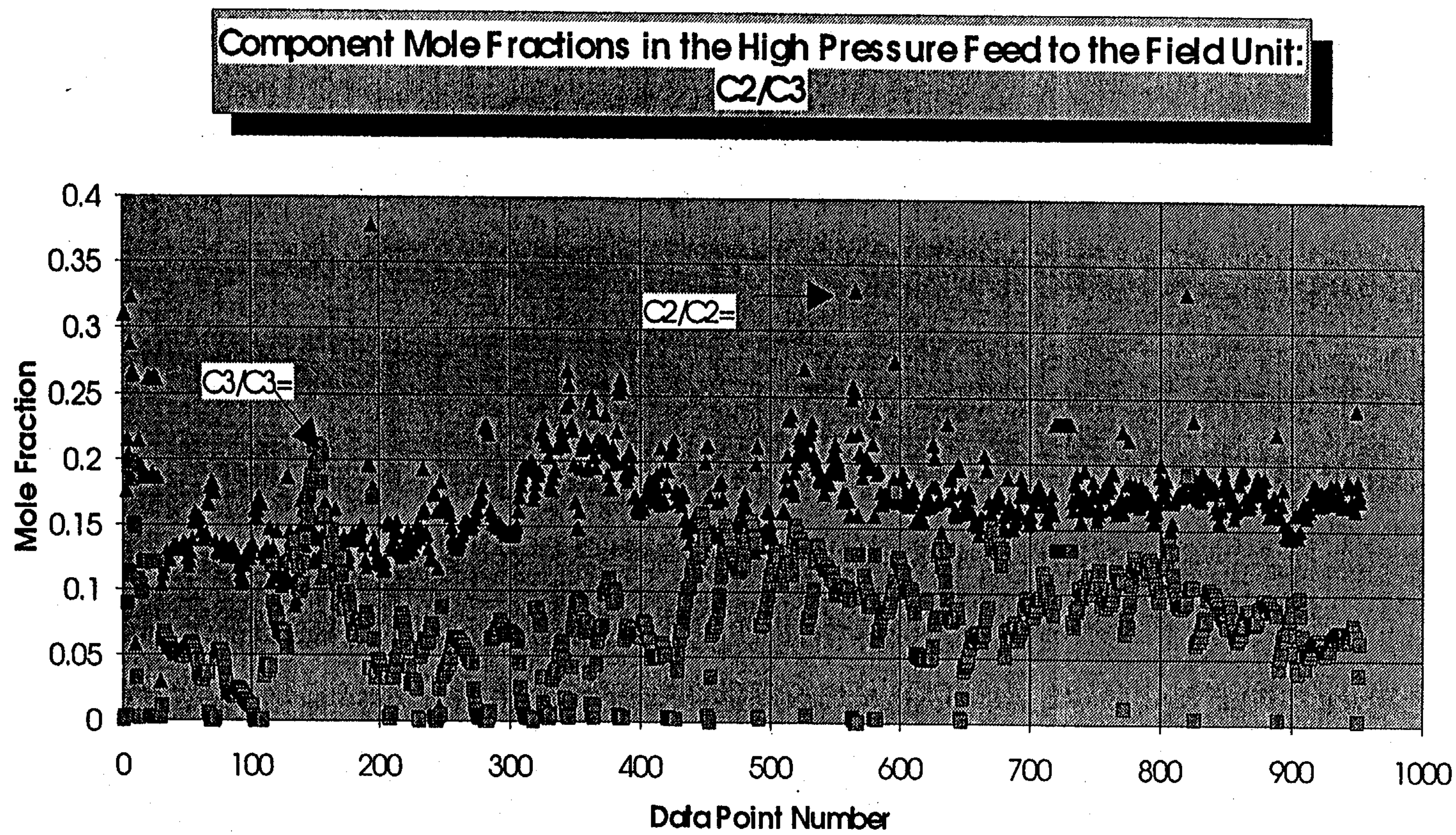
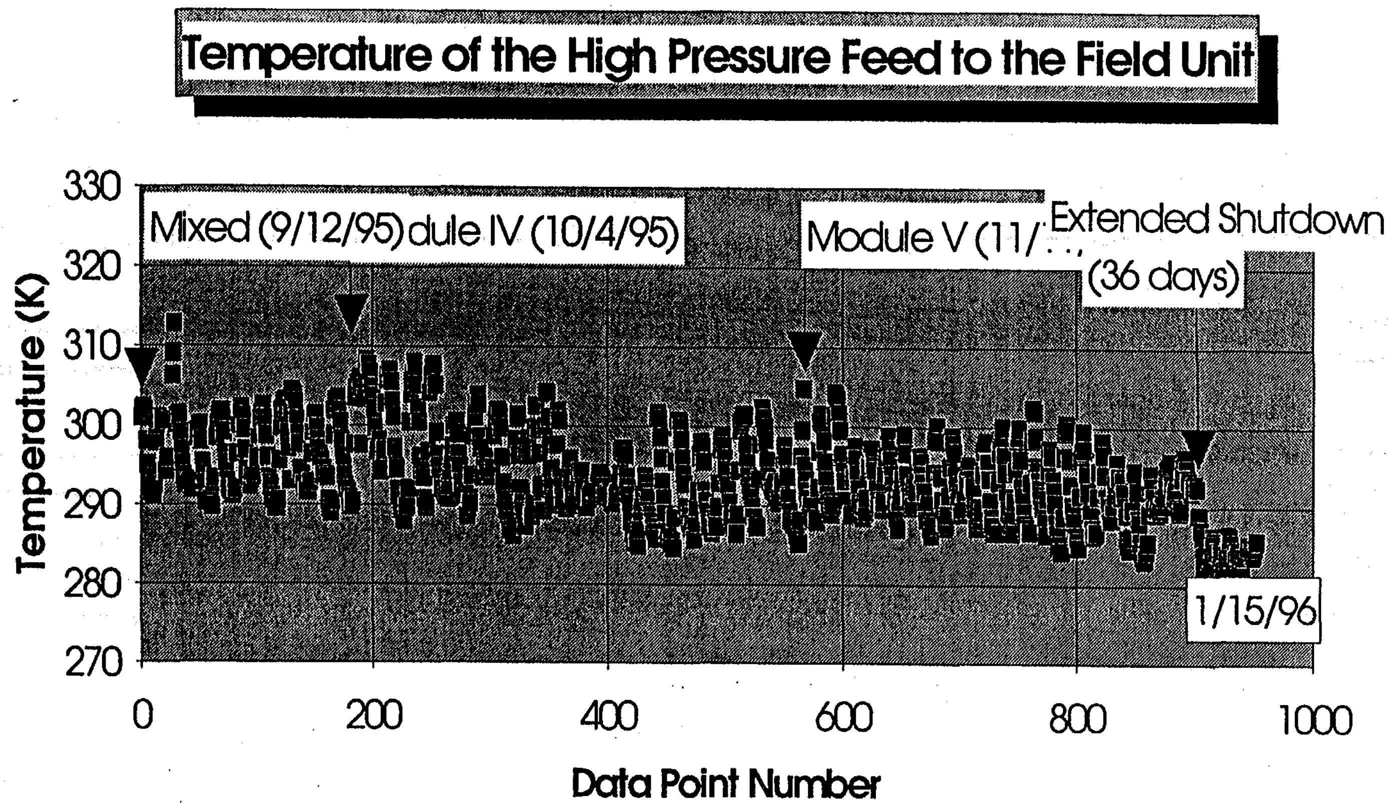

Component Mole Fractions in the High Pressure Feed to the Field Unit:
C2/C3
C2/C2=
C3/C3=
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Mole Fraction
0
100
200
300
400
500
600
700
800
900
1000
Data Point Number

Figure 15



Temperature of the High Pressure Feed to the Field Unit
Mixed (9/12/95)
dule IV (10/4/95)
Module V (11/
Extended Shutdown
(36 days)
1/15/96
Temperature (K)
330
320
310
300
290
280
270
0
200
400
600
800
1000
Data Point Number

Figure 16

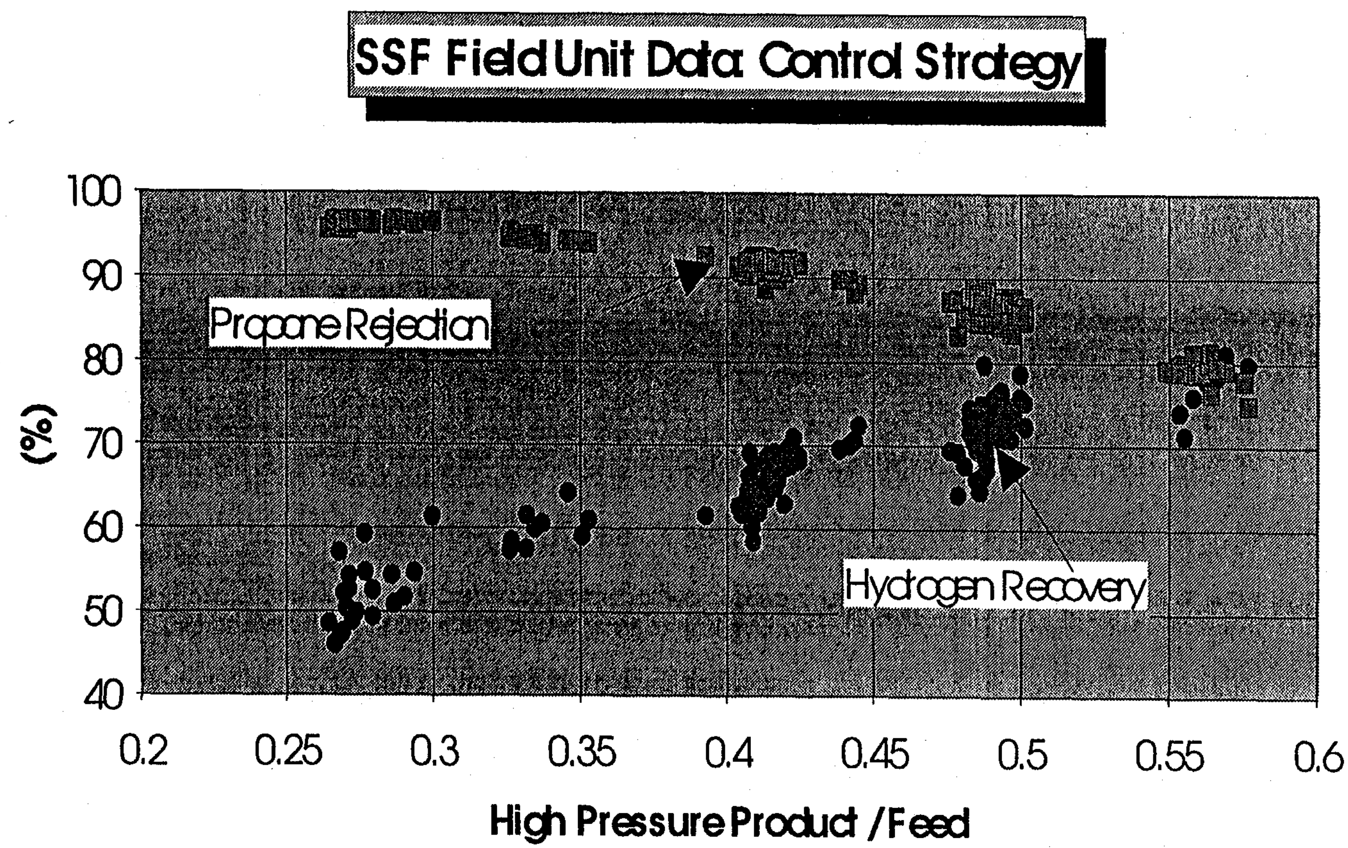
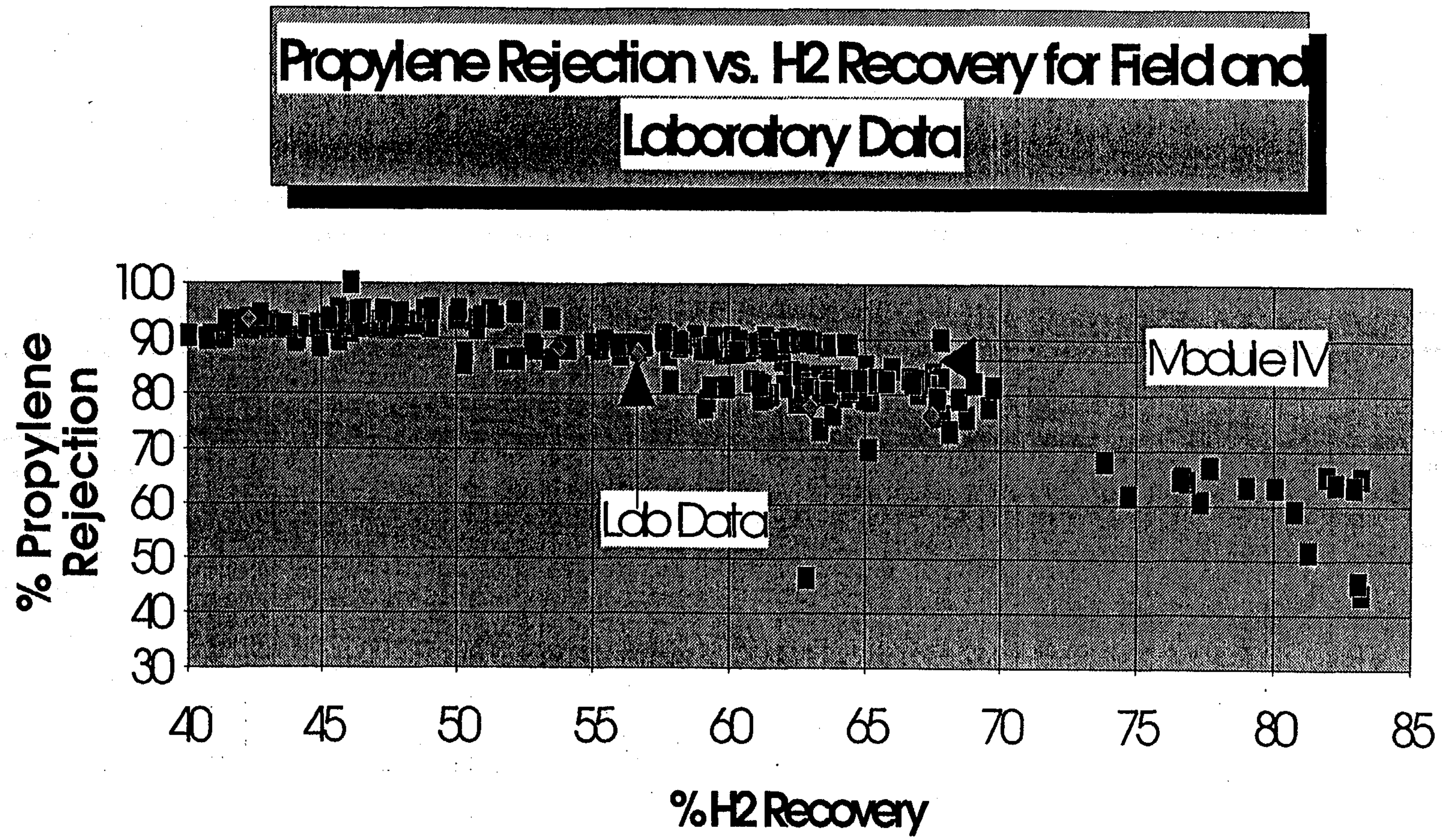
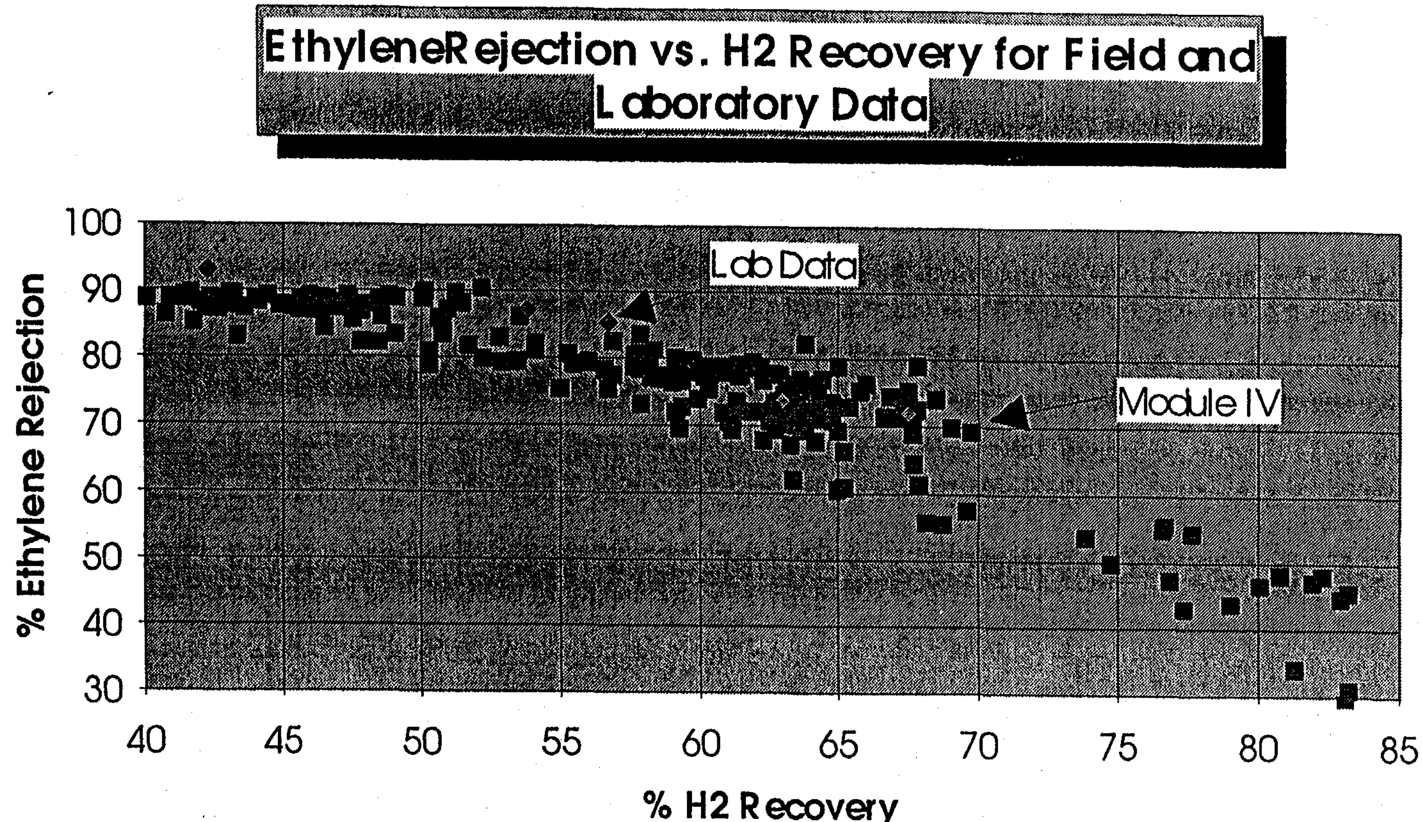

SSF Field Unit Data Control Strategy
100
90
80
70
60
50
40
(%)
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6
High Pressure Product /Feed
Propane Rejection
Hydrogen Recovery

Figure 17



Propylene Rejection vs. H2 Recovery for Field and Laboratory Data
% Propylene Rejection
100
90
80
70
60
50
40
30
40
45
50
55
60
65
70
75
80
85
% H2 Recovery
Module IV
Lab Data

Figure 18



EthyleneRejection vs. H2 Recovery for Field and Laboratory Data
Lab Data
Module IV
% Ethylene Rejection
100
90
80
70
60
50
40
30
40
45
50
55
60
65
70
75
80
85
% H2 Recovery

Figure 19

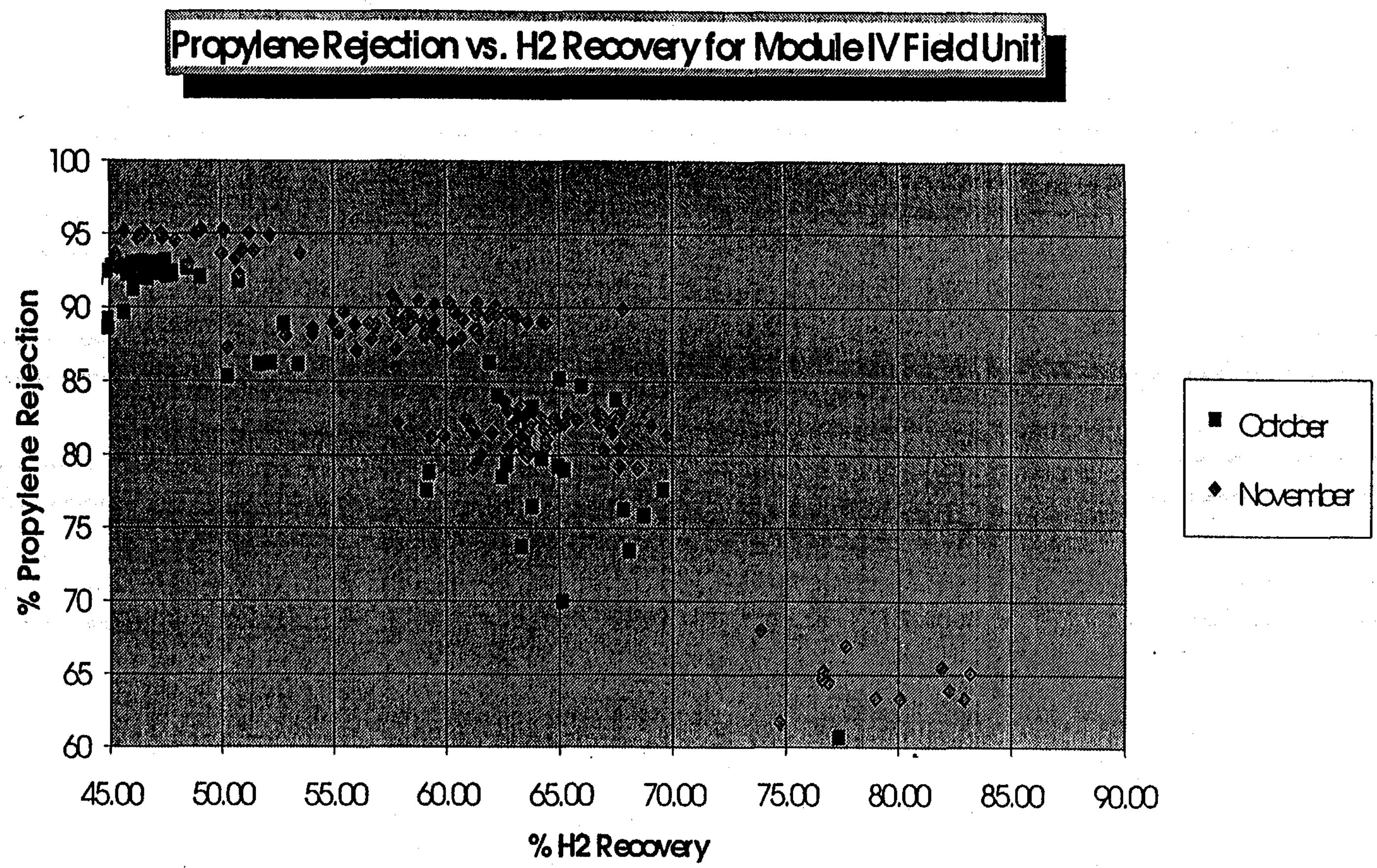
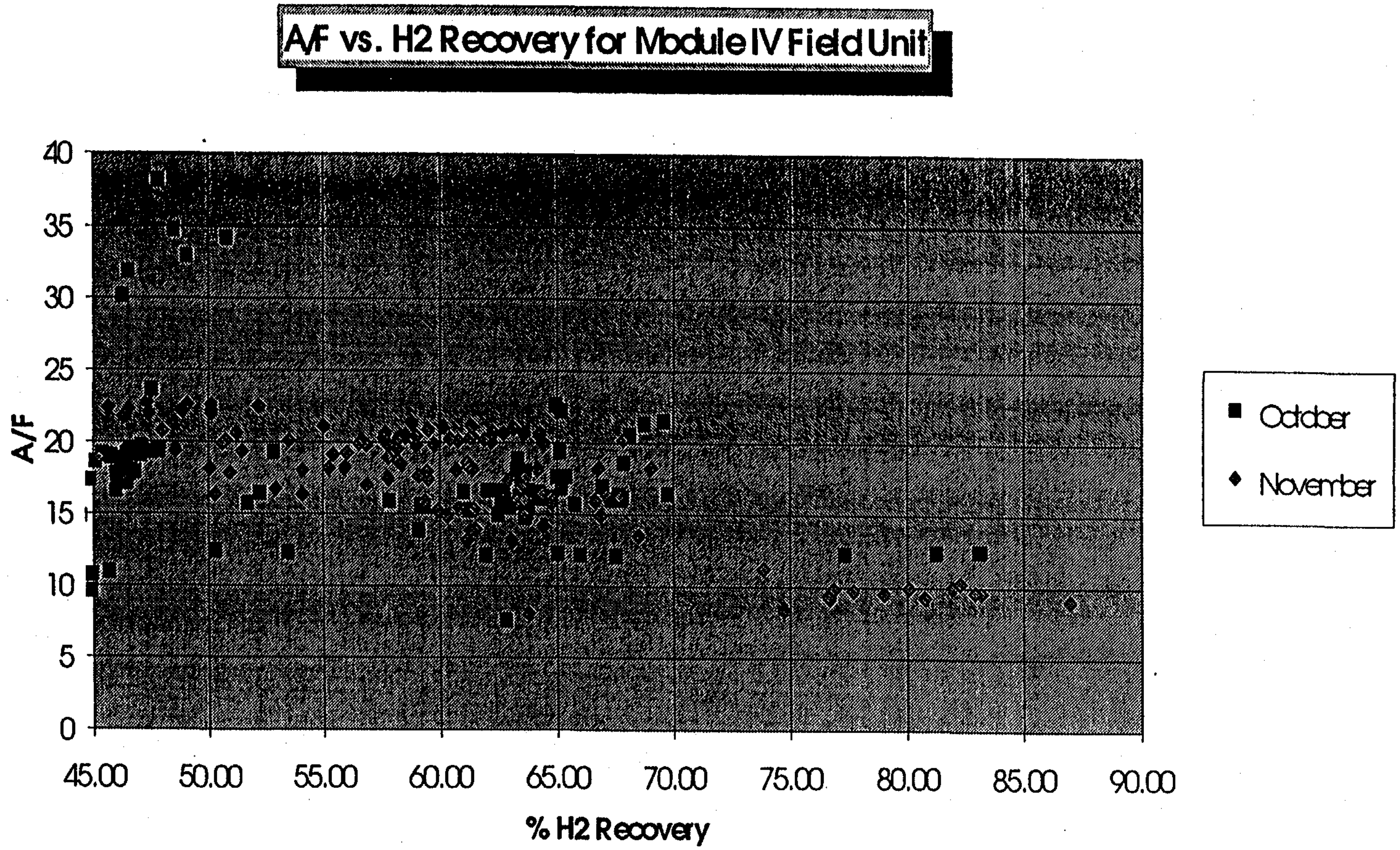

Propylene Rejection vs. H2 Recovery for Module IV Field Unit
100
95
90
85
80
75
70
65
60
% Propylene Rejection
45.00
50.00
55.00
60.00
65.00
70.00
75.00
80.00
85.00
90.00
% H2 Recovery
October
November

Figure 20


A/F vs. H2 Recovery for Module IV Field Unit
A/F
40
35
30
25
20
15
10
5
0
45.00
50.00
55.00
60.00
65.00
70.00
75.00
80.00
85.00
90.00
% H2 Recovery
October
November