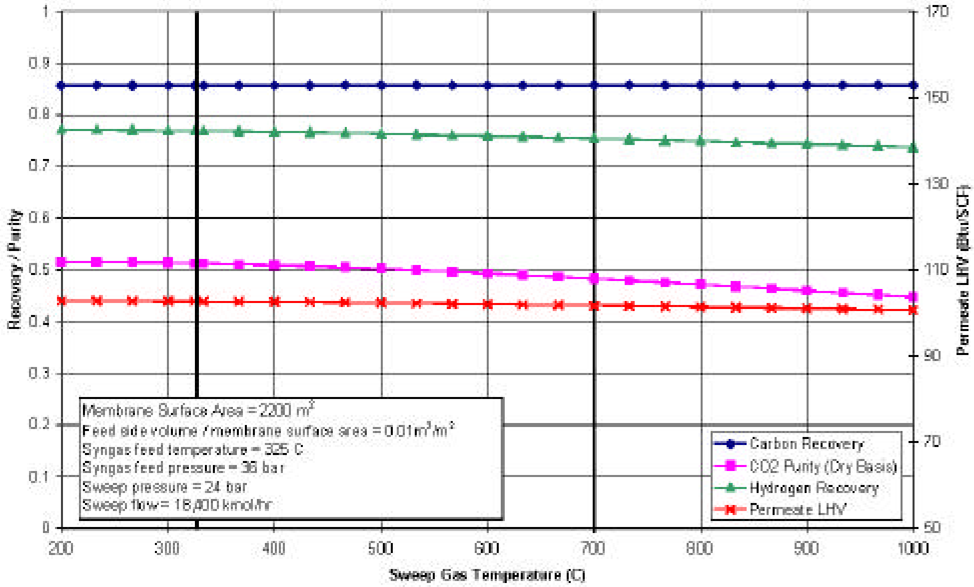
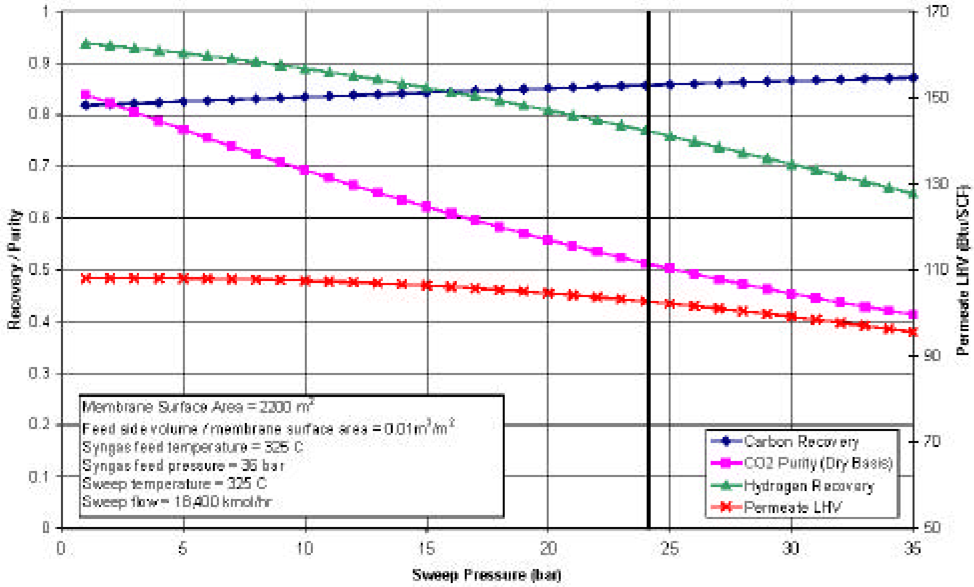
Figure 3-10
Sweep Gas Temperature Sensitivity
Silica Membrane - Default Values



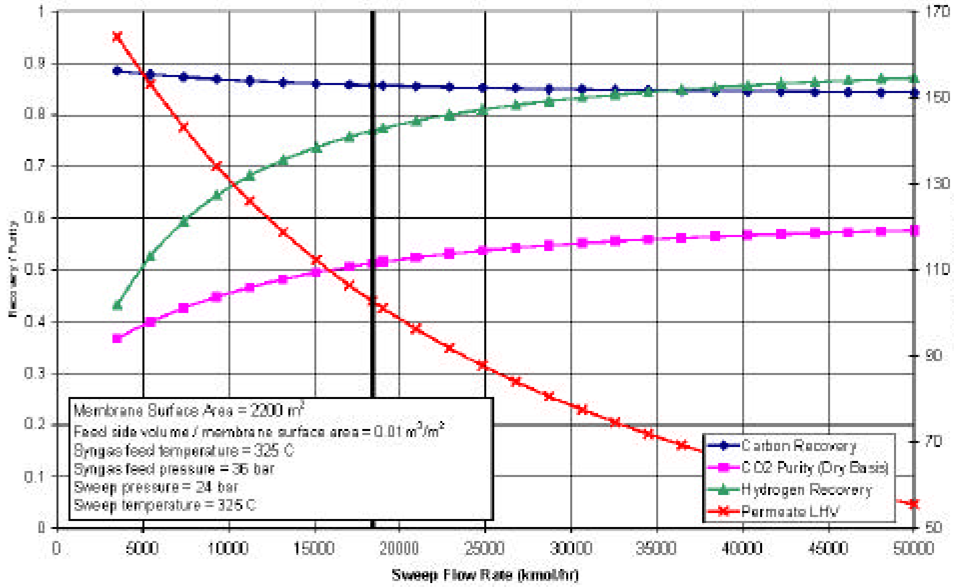
As seen in Figure 3-10, the carbon recovery, carbon dioxide purity, hydrogen recovery and permeate LHV are relatively constant over the range of sweep temperatures studied. For the gasification plant, a lower sweep feed temperature increases the amount of steam that can be produced for power generation. Therefore, the sweep temperature was set at the lowest possible temperature of 215°C (based on a maximum temperature differential between the syngas feed and permeate of 100°C). (However, as the process design progressed, the sweep temperature was later changed to 315°C due to heat recovery issues downstream of the MWGS reactor.)

Figure 3-11
Sweep Pressure Sensitivity
Silica Membrane - Default Values



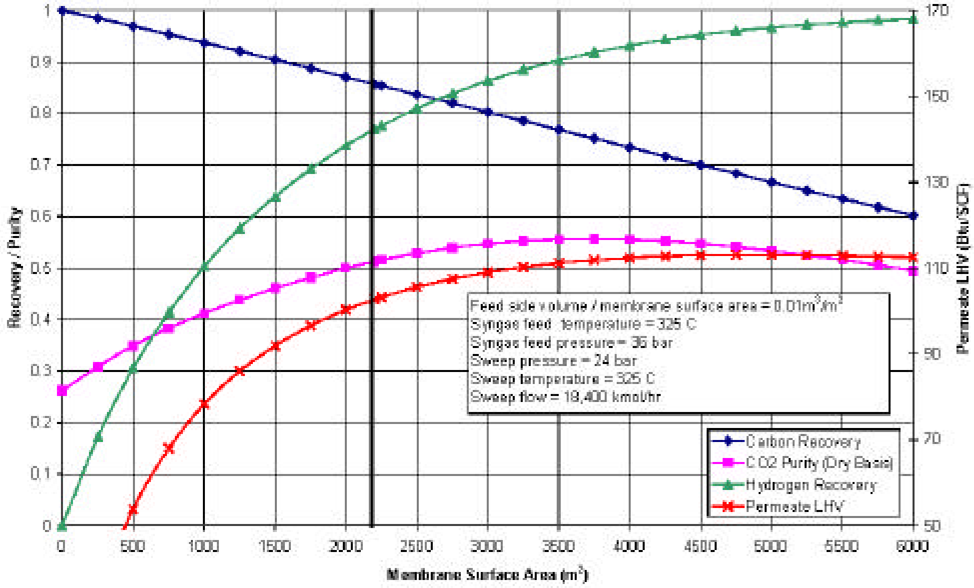
As the sweep pressure increases (decreasing driving force for hydrogen permeability – opposite effect of increasing syngas feed pressure), the carbon recovery increases while the hydrogen recovery decreases (at approximately four times the rate as that for the carbon recovery increase) as seen in Figure 3-11. The lowest possible sweep pressure is optimum for hydrogen permeability; however, a permeate pressure of 1 bar (minimum specified by ECN) was not sufficient pressure for the injection of the hydrogen-rich fuel into the existing fuel system for the current furnaces/boilers. Therefore, the sweep pressure was set to 5 bara per CCP's direction based on the fuel pressure requirements. The pressure differential over the membrane of 30 bar is below the maximum of 100 bar stipulated by ECN. (However, it was found later by CCP that the sweep pressure could be lowered to 3 bara to increase the hydrogen flux driving force.)

Figure 3-12
Sweep Flow Rate Sensitivity
Silica Membrane - Default Values



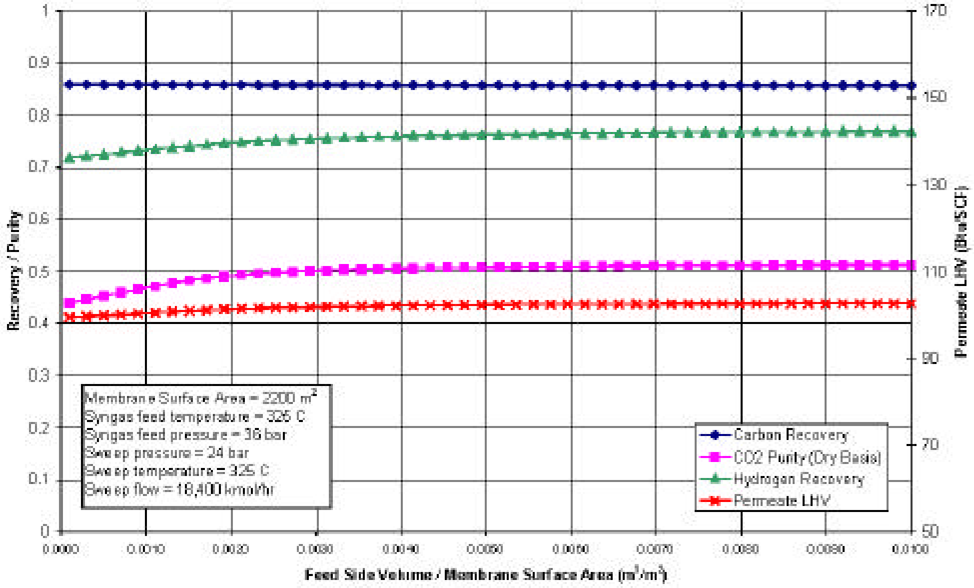
As the sweep flow rate increases, the hydrogen recovery increases; however, this adversely affects the permeate heating value as seen in Figure 3-12. Also, the nitrogen flow rate for sweep gas is limited by the amount of nitrogen (~12,700 kmol/hr) available from the Air Separation Unit. The nitrogen can be supplemented by steam to decrease the membrane surface area required for the same carbon recovery. However, this option was not pursued for the sensitivity studies as preliminary calculations show that for a 3-4% reduction in surface area, the power generation decreases by 6-7 MWe. (However, steam was used later in the process design to meet performance targets for the MWGS reactor). The sweep rate was set to 3400 kmol/hr so that the heating value of the permeate was 192 Btu/SCF (LHV).

Figure 3-13
Membrane Surface Area Sensitivity
Silica Membrane - Default Values



As the membrane surface area increases (increasing hydrogen permeability), the carbon recovery decreases while the hydrogen recovery increases (at approximately three times the rate as that for the carbon recovery decrease) as shown in Figure 3-13. Membrane surface areas greater than 6000 m^2 were not evaluated because of problems with the speed of the convergence of the model at higher surface areas. As the membrane research are still at the bench scale level, no recommendations on the optimum size of the membrane system could be made at this time. Therefore, based on the recommended values for the other input variables, the membrane surface area was optimized to maximize carbon recovery without considering economics.

Figure 3-14
Feed Side Volume / Membrane Surface Area Sensitivity
Silica Membrane - Default Values



The carbon and hydrogen recoveries, carbon dioxide purity and permeate heating value are insensitive to the feed side volume/membrane surface ratio for the range studied as seen in Figure 3-14. The feed side volume/membrane surface area ratio was set to 0.0015 m^3/m^2 based on input from ECN, which resulted in an even temperature distribution and also increased the speed of the model convergence. (However, later estimates showed a feed side volume/membrane surface area ratio of 0.10 m^3/m^2 resulted in higher carbon recovery (higher ratios increase catalyst volume thus promoting the shift reaction) so later estimates were based on the higher ratio.)

The allowable ranges for the input variables and recommended optimum operating conditions for the silica membrane are shown in Table 3-5.

Table 3-5
Allowable Range and Recommended Values for Input Variables
Silica Membrane
(Based on preliminary sensitivity analysis)

Variable	Allowable Range	Recommended Values
Syngas feed temperature, °C (Catalyst temperature range)	200 – 1000 (300-450)	315
Syngas feed pressure, bara	1 – 100	35
Sweep temperature, °C	200 – 1000	215
Sweep pressure, bara	1 – 100	5
Sweep flow rate, kmol/hr	Maximum available is ~12,700 kmol/hr	3400
Membrane surface area, m^2	None	3100
Feed side volume/membrane surface area ratio, m^3/m^2	0.003 – 0.2	0.0015

The final results for the recommended case are shown in Table 3-6.

Table 3-6
Recommended Value Case
Silica Membrane

Carbon Recovery, %	72.7
Hydrogen Recovery, %	95.9
CO_2 Purity, mol% (dry)	85.4
Permeate LHV, Btu/SCF (LHV)	172.5

Note that the carbon dioxide purity (85.4 mol%, dry) is below the target value of 90 mol%, dry and the carbon recovery is below the target of 90%. Sensitivity cases were developed, which showed that an hydrogen/carbon dioxide selectivity of fifty resulted in a carbon recovery of 90% for the silica membrane.

3.4.2 Sensitivity Studies Results for First Version Membrane Simulation Model for the Zeolite Membrane

Similar to the silica membrane, sensitivity runs were developed for the zeolite membrane based on preliminary permeation tests. The syngas feed composition for the zeolite membrane sensitivity runs were the same as that for the silica membrane (see prior section). The default values used are shown in Table 3-7. Again, the permeances were based on experimental tests with sweet syngas and the feed to the computer model was sour syngas.

Table 3-7
Default Values
Zeolite Membrane

Variable	Default Value
Syngas feed temperature, °C	350
Syngas feed pressure, bara	36
Sweep temperature, °C	350
Sweep pressure, bara	24
Sweep flow rate, kmol/hr	18,400
Membrane surface area, m^2	2,200
Feed side catalyst volume/membrane surface area ratio, m^3/m^2	0.01

The results of the computer model for the case with the default values are shown in Table 3-8.

Table 3-8
Default Value Case
Zeolite Membrane

Carbon Recovery, %	96.2
Hydrogen Recovery, %	10.5
CO_2 Purity, mol% (dry)	30.4
Permeate LHV, Btu/SCF (LHV)	21

The Default Value Case is shown on the sensitivity graphs (Figures 3-14 to 3-20) as a vertical straight line for reference. An optimum operating case for the zeolite membrane was not done as the sensitivity studies showed a fairly poor performance for the membrane. Therefore, these sensitivity graphs were sent to the University of Cincinnati to give them an idea of the preliminary performance of zeolite membrane so that they could investigate options to improve their system.

Figure 3-14
Syngas Feed Temperature Sensitivity
Zeolite Membrane

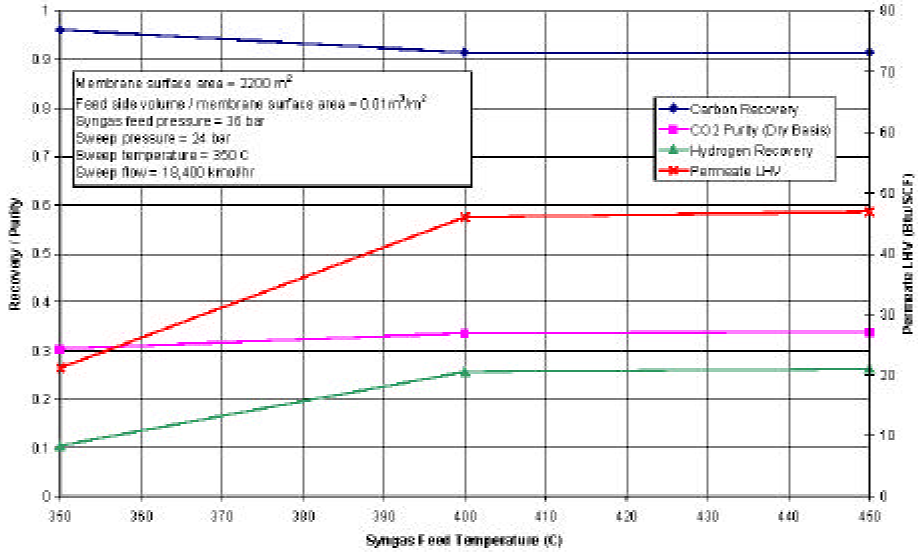


Figure 3-15
Syngas Feed Pressure Sensitivity
Zeolite Membrane

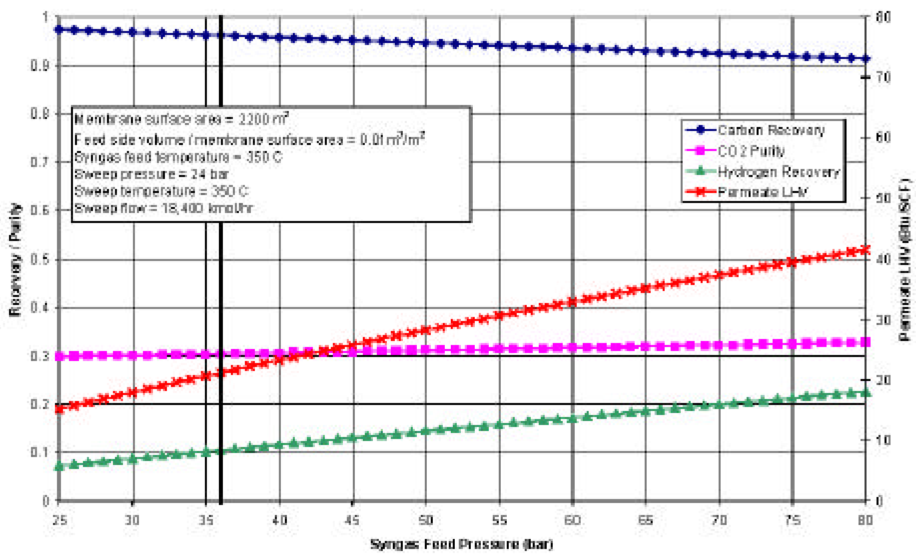


Figure 3-16
Sweep Gas Temperature Sensitivity
Zeolite Membrane

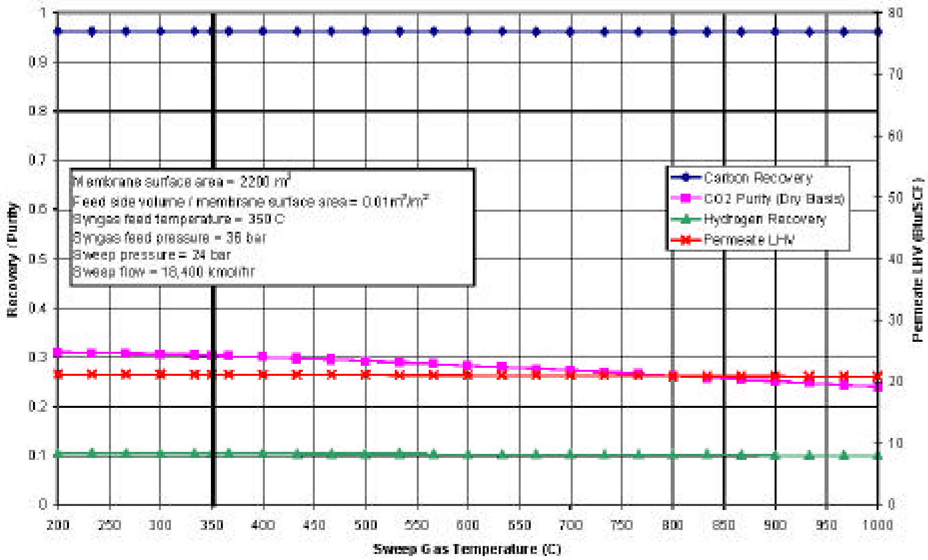


Figure 3-17
Sweep Pressure Sensitivity
Zeolite Membrane

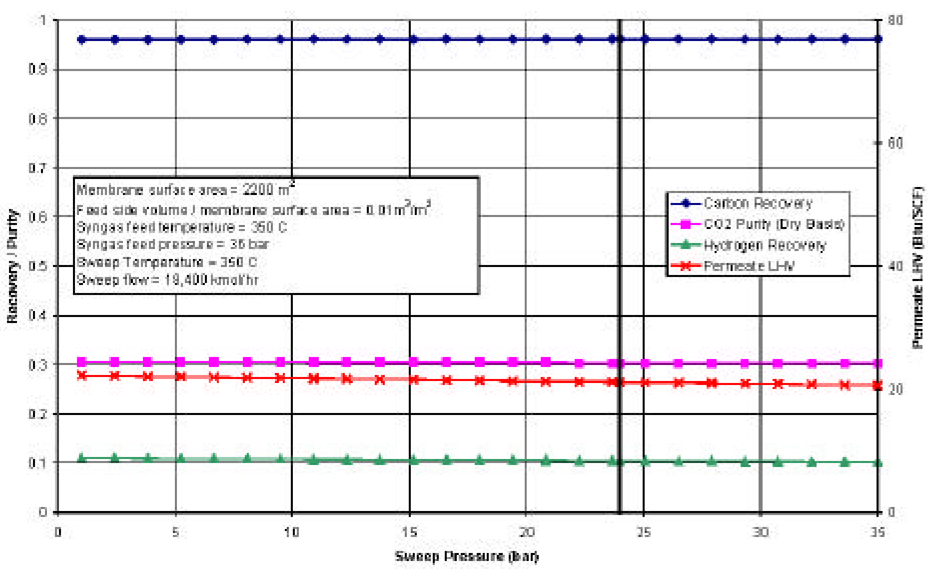


Figure 3-18
Sweep Flow Rate Sensitivity
Zeolite Membrane

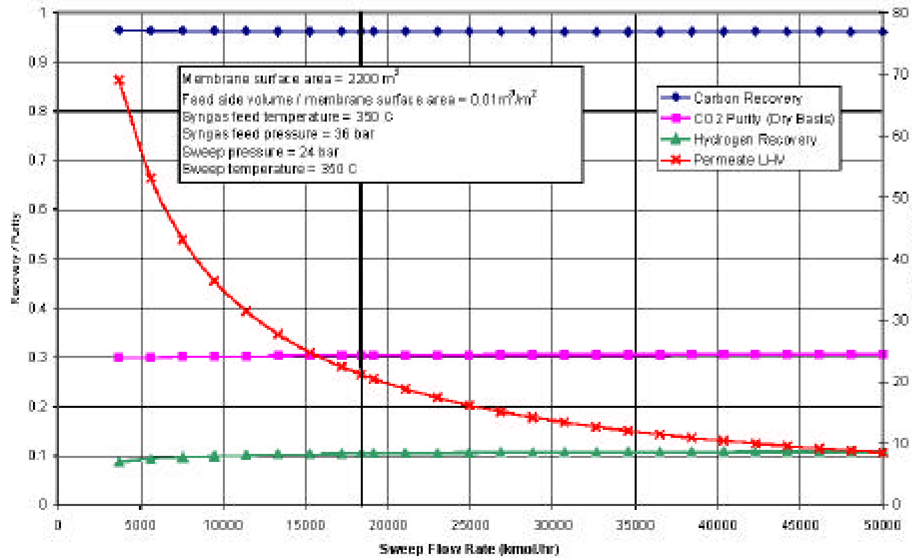


Figure 3-19
Membrane Surface Area Sensitivity
Zeolite Membrane

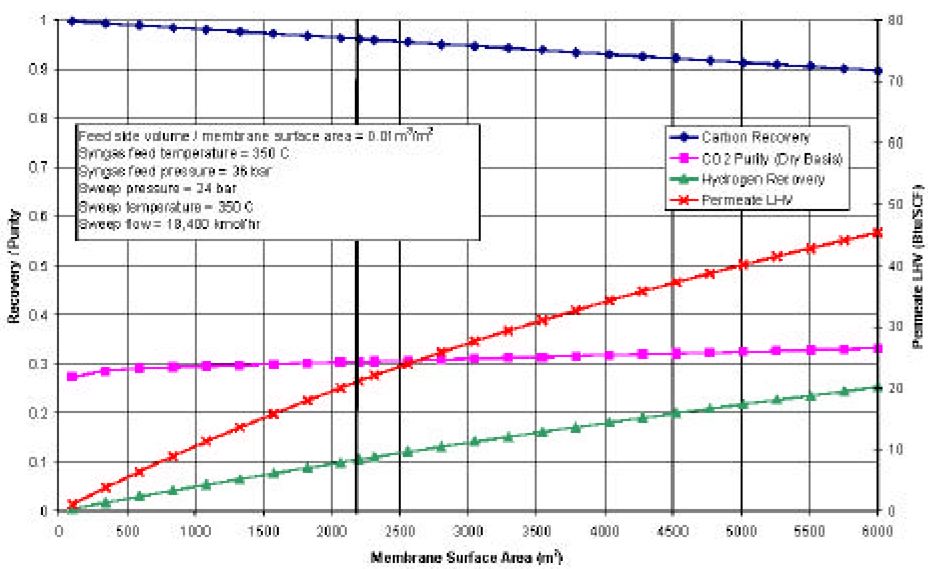
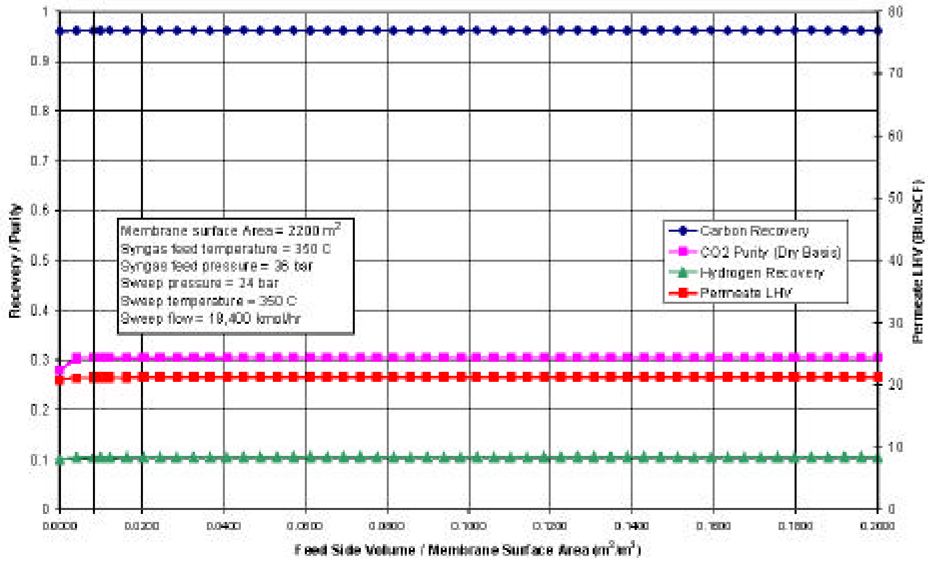


Figure 3-20
Feed Side Volume / Membrane Surface Area Sensitivity
Zeolite Membrane



3.4.3 Performance Results for the Final Version Membrane Simulation Model

The performance for all the membranes are shown in Table 3-9. All membranes had a sour syngas as the feed for the computer model. However, MWGS reactor performances with permeances based on experimental data with a sweet syngas feed are denoted as "Sweet." The syngas feed temperatures were set to 315°C except for the metal ceramic composite membrane based on experimental data with sour syngas (due to poor performance of the membrane at lower temperatures) and the Pd-Alloy membranes (due to the permeance being reported at 350°C with no temperature correction factor). All four membranes have the syngas feed and sweep at 34 barg and 2 barg, respectively.

As the table shows, the metal ceramic composite membrane has infinite selectivity so that the carbon recovery is 100%. As the permselectivity of H_2/CO_2 decreases, the carbon recovery decreases. The three other membranes did not meet the target carbon recovery of 90% as the permselectivities of H_2/CO_2 were too low.

The table also shows the pre-exponential factors and activation energies supplied by the membrane vendors. Numerous membrane data were received from the vendors; therefore, for clarification the date for the membrane data is provided as the last item on the table.

Based on the fact that the metal ceramic composite membrane was the only membrane to meet the carbon recovery target, CCP decided that the overall gasification plant performance be estimated based on the metal ceramic composite membrane with permeances from experimental tests with sweet syngas. Therefore, for Phase I, the performance of the sulfur tolerant MWGS reactor was estimated based on permeances derived from experiments with a sweet syngas feed.

In Phase II of the project, the work will again be based on the metal ceramic composite membrane with permeances derived from experiments with a sweet syngas feed. (The sulfur tolerant MWGS reactor will not be pursued due to low hydrogen flux when sulfur compounds are present.) However for Phase II, the configuration of the gasification plant will be revised in order for the hydrogen sulfide and carbonyl sulfide content in the feed to the MWGS reactor to be less than a 10 ppmv. The tasks for Phase II will include:

Eltron Research Inc.

- Develop a laboratory proof-of-concept MWGS reactor.

SOFCo

- Design and estimate the cost of a commercial scale MWGS reactor.

Fluor

- Design the gasification plant for a sweet syngas feed to the metal ceramic composite membrane WGS reactor.
- Incorporate design considerations into the gasification plant based on input from SOFCo.
- Estimate heat and material balance of the entire plant.
- Estimate the plant performance.
- Develop sized equipment list.
- Develop process flow diagrams.
- Develop utility summary.
- Prepare a report.

Table 3-9
Membrane Water Gas Shift Reactor Performance Summary

Membrane Vendor	Eltron		Colorado School of Mines/TDA		ECN	University of Cincinnati
Membrane Type	Metal Ceramic Compos.		Pd-Alloy		Silica	Zeolite
Syngas Feed for Experimental Tests (to determine permeances)	Sweet	Sour	Sweet	Sour	Sour (Note 4)	Sour (Note 4)
Syngas feed temperature, C	315	450	350		315	315
Syngas feed pressure, barg	34					
Sweep gas pressure, barg	2					
Carbon recovery,%	100.0		73.5	45.6	35.1	12.4
CO2 purity, dry %	90.2	90.0	90.0	90.0	90.0	86.6
Hydrogen recovery, %	95.3	95.2	96.9	97.8	95.9	98.9
Hydrogen LHV, Btu/SCF (Note 1)	149.7	149.8	150.0	150.7	149.8	150.1
Hydrogen purity, % (after water condensation)	54.7	54.7	54.5	54.6	53.0	54.4
Permeate H2, kmol/hr	11582.9	11582.4	11778.2	11883.7	11653.7	12023.3
H2 flux, mol/m2-sec	0.19	0.08	0.35	0.15	0.22	0.17
H2 permeance, mol/m^2-sec-Pascal	n/a		5.80E-07	2.38E-07	1.77E-07	3.27E-07
H2 pre-exponential factor, mol/m^2-sec-Pascal	n/a		5.80E-07	2.38E-07	4.93E-07	1.46E-07 (Note 2)
H2 pre-exponential factor, mol/m^2-sec-Pascal^0.5	2.87E-02	7.14E+08	n/a		n/a	n/a
H2 Activation Energy, J/mol	24896	186000	0		5007	-3941
H2 permeance, mol/m^2-sec-Pascal^0.5	1.966E-04	2.650E-05	n/a		n/a	n/a
H2:CO2 permselectivity at feed conditions	infinite	infinite	13.3	5.5	4.7	2.6 (Note 2)
Membrane area required, m2	17,325	39,000	9,400	21,500	15,000	19,400
Nitrogen sweep gas required, kgmol/hr	9,100	9,100	7,800	5,000	7,000	4,500
Steam sweep gas required, kgmol/hr	8,800	20,000	-	20,000	230,000	8,000
Date Membrane Data Received	Jan. 21, 2003		Jan. 16, 2003	Jan. 16/March 5, 2003	Feb. 26, 2003	March 10, 2003

Notes:
(1) Cooling of fuel to 95 F was required to meet LHV requirement
(2) Permeance at 10 bar.
(3) n/a = not applicable
(4) See preliminary sensitivity studies for performance of the silica and zeolite membrane with sweet syngas.

4.0 GENERAL DESIGN CRITERIA

4.1 Introduction

This section presents the General Design Criteria for the Membrane Water Gas Shift Reactor Study for CO_2 Capture Project. The purpose of this document is to ensure a degree of uniformity of criteria for the design of the plant.

4.1.1 Overview

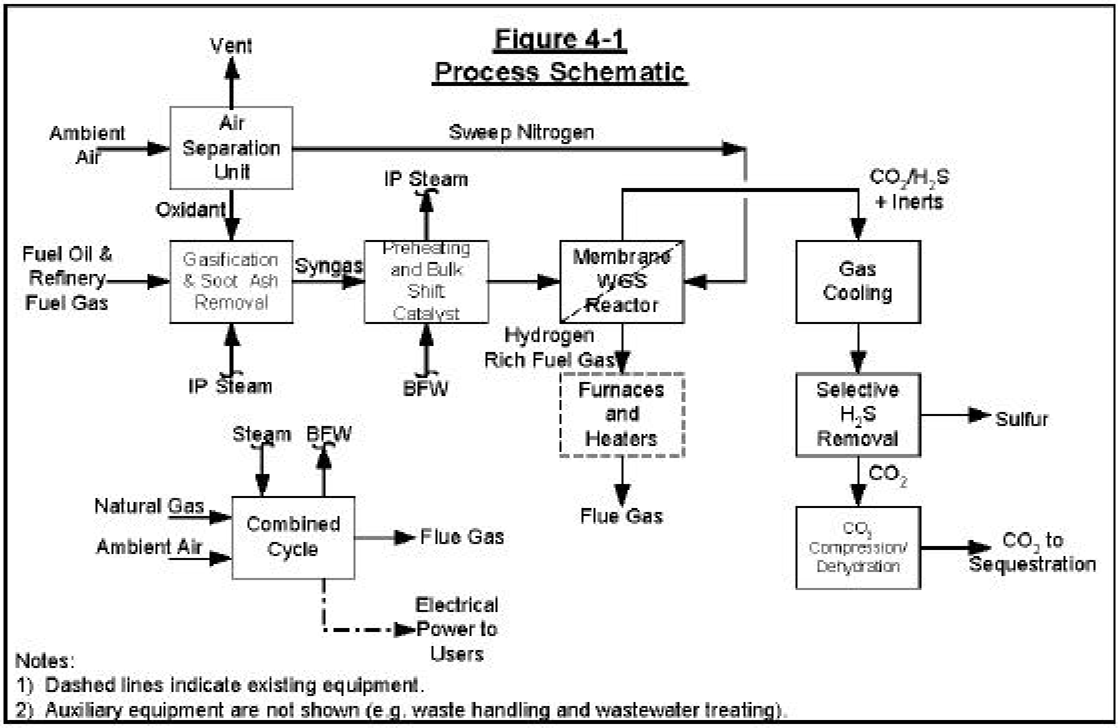
The scope of this study is to develop a conceptual process design for the gasification of residual oil and refinery fuel gas to produce a hydrogen rich fuel (carbon-free fuel) for the use in the existing refinery and petrochemical furnaces and heaters. The syngas from the gasifier is fed to a bulk shift catalyst where the carbon monoxide and water are converted to hydrogen and carbon dioxide. The shifted syngas is then fed to a sulfur tolerant membrane water gas shift (MWGS) reactor system, which provides additional conversion of the remaining carbon monoxide then separates the product hydrogen from the product carbon dioxide. The hydrogen rich stream is fired in the existing equipment producing a flue gas, which is relatively free of carbon dioxide. The carbon dioxide rich stream from the MWGS reactor is treated to remove sulfur compounds and compressed for geologic sequestration. The target carbon dioxide purity is 90 mol%, dry.

The site location is at the BP facilities (includes refinery, power station and chemicals plant) at Grangemouth.

4.1.2 Project Facilities

A process schematic for the gasification of a heavy feedstock to produce hydrogen rich fuel gas using the membrane WGS reactor is depicted in Figure 4-1. The syngas from the gasifier is cleaned of particulates, preheated, shifted in a bulk shift catalyst then fed to the WGS reactor. The membrane removes product hydrogen from the reactor, facilitating higher conversion of the carbon monoxide and water to hydrogen and carbon dioxide at a given temperature. If sufficient conversion is achieved, the non-permeate comprises mainly carbon dioxide with low concentrations of hydrogen sulfide, methane, nitrogen and argon.

The electrical power for the plant is provided by a natural gas fired combined cycle.



4.1.3 General Criteria and Philosophy

a) The plant is designed to recover two (2) million tonnes per year of CO_2 (100% basis and 330 days per year operation with a carbon recovery of 100% for the membrane WGS reactor). This target quantity reflects the overall aims of the Grangemouth site, i.e. to capture 50% of the CO_2 from across the complex.

b) The plant is designed to be self sufficient in most utilities including electrical power. The firewater is assumed to be provided by the existing site infrastructure. (This assumption for the firewater is the same as the design in the BP Grangemouth CO_2 Capture Report.)

4.1.4 Battery Limits Definition

The following commodities are supplied to the plant at the battery limits:

- Residual oil feed
- Refinery fuel gas
- Natural gas
- Make up water
- Ambient air