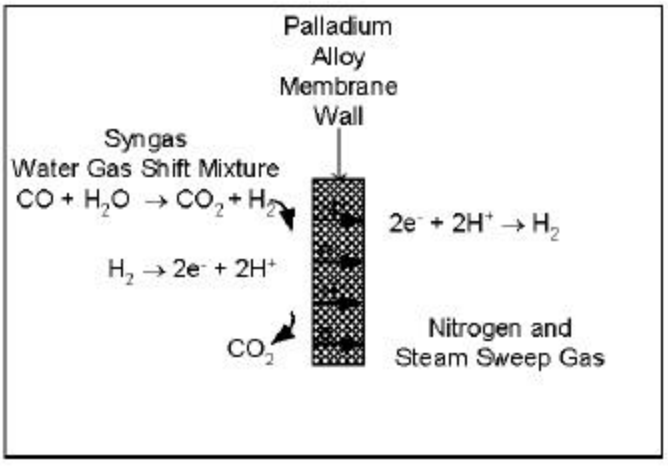
However, it was found that the catalyst for adsorption and dissociation was poisoned by the level of hydrogen sulfide in the syngas feed to the MWGS reactor (see section 3.4.3 for results with permeances based on experimental data with a sour syngas feed). The project schedule did not permit Eltron Research Inc. to continue their efforts in troubleshooting this problem. For more details on the metal ceramic composite membranes, see the "Final Report: Integrated Water-Gas Shift/Hydrogen Transport Membrane Technology for Simultaneous Carbon Dioxide Capture and Hydrogen Separation" prepared by Eltron Research Inc. dated February 2003.

3.2.2 Palladium Alloy Membrane

The palladium alloy composite membrane was offered by Colorado School of Mines (CSM) in partnership with TDA Research, Inc. in Golden and Wheat Ridge, Colorado. The hydrogen transport concept for the Pd Alloy membrane is shown in Figure 3-3.

Figure 3-3
Hydrogen Transport for the Palladium Alloy Membrane



Palladium alloys were chosen as they have higher permeability and hydrogen fluxes (as much as two to nine times increase than Palladium alone). The Palladium (Pd)/Copper (Cu) alloy was selected because it was cheaper than other alloys considered; in addition to being resistant to hydrogen sulfide and robust during thermal cycling.

The first membrane test consisted of measuring hydrogen to nitrogen selectivity and it was found that the selectivity was lower than expected. Leak testing and visual inspection indicated that cracks and chips (boulders and pinholes) were responsible for the poor selectivity.

Methods were developed for addressing the leaks, such as metal brazing and re-glazing.

To identify effects of individual components in the syngas feed on the membrane performance, the membranes were exposed to different binary gas mixtures. These tests were then followed by a test with a sulfur-free syngas. The performance of the membrane based on permeances derived from experimental tests with sweet syngas are shown in section 3.4.3. (Note that the actual feed basis in the computer model for the MWGS reactor is sour syngas.) It was determined that the hydrogen was transported through the membrane as atomic hydrogen; however, carbon dioxide and carbon monoxide were also transporting through due presumably to surface diffusion mechanisms. It was speculated by CSM/TDA that the carbon dioxide and carbon monoxide first chemisorbs on the surface and then spills over to the permeate side through defects by consequent adsorption and desorption.

To increase the selectivity of the membrane, CSM/TDA tried to develop thicker membranes (ten to twelve microns versus three to four microns thickness). These membrane demonstrated higher selectivities; however, when exposed to hydrogen sulfide, the performance of the membranes deteriorated greatly. CSM/TDA tried, unsuccessfully, within the permitted schedule to develop a performance for a membrane with a sour syngas feed.

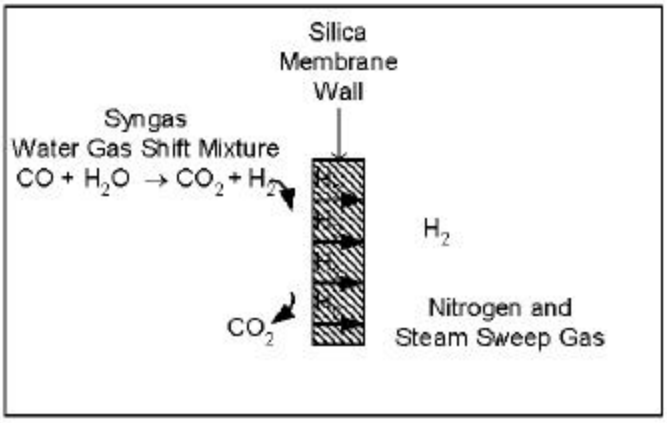
Therefore, CSM/TDA advised Fluor to develop an estimate for the performance of the membrane with a sour syngas feed by derating the results of the membrane performance with sweet syngas. Per CSM/TDA's instructions, the hydrogen flux was decreased to 70% of its original flow to account for the effect of the hydrogen sulfide on the hydrogen flux. The membrane performance with permeances based on experimental data with a sour syngas feed is shown in Section 3.4.3.

For more details, see the progress reports and memos prepared by Colorado School of Mines and TDA Research, Inc.

3.2.3 Silica Membrane

The silica membrane was offered by Energy research Centre of the Netherlands (ECN). The hydrogen transports through the silica membrane as molecular hydrogen. The mechanism is shown in Figure 3-4.

Figure 3-4
Hydrogen Transport for the Silica Membrane



Silica membranes have the advantage of being sulfur tolerant and having a low cost. However, the selectivity of the membrane was found to be low. The transport of all components through the membrane is governed by "activated diffusion." However, carbon dioxide also adsorbs on the membrane surface and is transported by surface diffusion as well. In the temperature range examined, the surface diffusion is stronger than the activated diffusion.

Sensitivity studies were performed using the computer model for the silica membrane to determine the optimum conditions for the MWGS Reactor and the results are shown in Section 3.4.1. The permeances for these sensitivity runs were based on experimental data with sweet syngas; however, the actual feed basis for the computer model of the MWGS reactor was a sour syngas. In addition, the membrane performance with permeances based on experimental data for a sour syngas feed is shown in Section 3.4.3. Both membrane performances were found to require higher hydrogen selectivity in order to meet project specifications for the product streams.

For more details on the silica membranes, see the progress reports and memos prepared by ECN.

3.2.4 Zeolite Membrane

The zeolite membrane was offered by the University of Cincinnati. The hydrogen transports through the zeolite membrane as molecular hydrogen and is analogous to the silica membrane (see previous section for silica membrane).

Zeolite membranes have the advantage of being sulfur tolerant and thermally stable. Sample membranes were prepared by dip coating

followed by template-free secondary growth. These membranes were first characterized by xylene pervaporation experiments to verify the extent of intracrystalline pores. P-xylene molecules were smaller than the crystalline pores while m- and o-xylene molecules were larger. A good separation of the p-xylene molecule indicated a good fabrication process for the membrane.

As with the silica membrane, sensitivity studies were performed for the zeolite membrane to determine the optimum conditions for the MWGS reactor and those results are shown in Section 3.4.1. Again, the permeances for these studies were based on experimental data with a sweet syngas. Further tests were performed with a syngas mixture and the membrane performance based on permeances from experimental tests with a sour syngas feed are shown in Section 3.4.3. Similar to the silica membrane, both membrane performances were found to require higher hydrogen selectivity in order to meet project specifications for the product streams.

For more details on the zeolite membranes, see the progress reports and memos prepared by University of Cincinnati.

3.3 Membrane Water Gas Shift Reactor Simulation Model

A computer model of the membrane water gas shift (MWGS) reactor was developed by Energy research Centre of the Netherlands (ECN) to determine the conditions (flow rate, composition, temperature and pressure) of the permeate and retentate for a specified membrane surface area. After consultations with the individual membrane vendors, the following hydrogen permeance equation was programmed into the model:

$$J = P_0 e^{-E/RT}\left(P_f^{\,n} - P_p^{\,n}\right)$$

where J = flux of hydrogen (gmol/m^2-s)
P_0 = pre-exponential permeance factor (gmol/m^2-s-Pa^n)
E = activation energy for hydrogen transport (J/gmol)
R = ideal gas constant (8.314 J/gmol-K)
T = temperature (Kelvin)
P = partial pressure of H_2 on the feed (f) and permeate (p) side (Pa)
n = exponent on driving force

Three computer, mathematical models (simplified, first version and final version) for integration into an Aspen Plus process computer simulator were developed by ECN. Three models were developed during the course of the project to avoid delays in the project schedule.

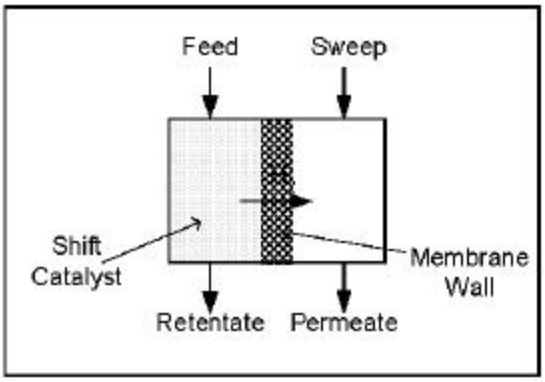
3.3.1 Simplified Simulation Model

The purpose of the simplified model was to give a functionality of the membrane WGS reactor and not to accurately predict the performance of

the MWGS reactor. The simulation to estimate the performance of the entire gasification plant could then be programmed using this simplified model so that the schedule was not delayed.

This simplified model required a commercial equation solver from the Numerical Algorithms Group (NAG) library. The model simulates a co-current membrane WGS reactor. The concept for the computer model is shown in Figure 3-5.

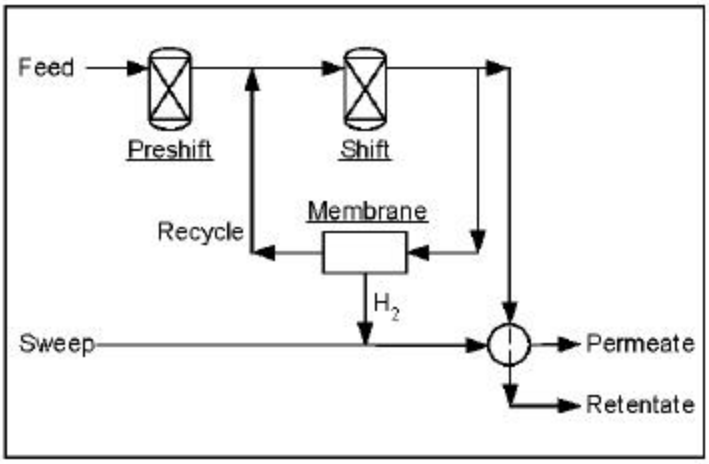
Figure 3-5
MWGS Reactor Simplified Model Concept



Syngas is fed to the feed side of the membrane. In this part of the reactor, a water gas shift reaction occurs. Simultaneously hydrogen diffuses through the membrane, enhancing the shift reaction by driving the reaction toward the products by the removal of the hydrogen. The hydrogen is transported through the membrane by a concentration driving force, which is increased by the use of a sweep gas to lower the hydrogen pressure on the permeate side of the membrane.

The model reactor is based on a combination of reactor, heat exchanger, splitter and mixers. The flow sheet for the simplified membrane model is shown in Figure 3-6.

Figure 3-6
Flow Sheet for Simplified Membrane Model



Aspen Plus was not able to model the shift reaction parallel with the hydrogen permeation. Therefore, an approach was chosen using a large recycling stream in which reaction and permeation take place. Due to this large recycling stream both processes can be considered to take place in parallel to each other. Heat exchange is assumed to take place after reaction and permeation. As a result, the effect of sweep gas temperature on the conversion is not taken into account.

The model is based on the following assumptions:

- No pressure drop on the feed and permeate side of the membrane
- No heat loss to the surroundings
- Thermodynamic equilibrium conditions for the shift reaction

The model is based on two design specs – the first spec adjusted the split fraction of the hydrogen in the membrane (split between the recycle and permeate streams) until the mole fraction of the hydrogen in the retentate converged to a given value. The second spec adjusted the sweep flow rate in order to obtain a desired driving force over the membrane (i.e. the hydrogen partial pressure at the feed side must always be larger than that on the permeate side) to avoid hydrogen flow back to the feed side. A FORTRAN block is also provided to check the driving force of the hydrogen partial pressure, which returned an error message or confirmation for proper conditions for hydrogen permeation.

Again, this model was not intended to predict the performance of the MWGS Reactor and only allowed for the permeation of hydrogen and no other components. Basically, this model was used as a "placeholder"

within the larger Aspen Plus simulation for the gasification plant so that the simulation efforts could proceed.

3.3.2 First Version Simulation Model

The first version of the membrane model was developed to estimate the performance of a counter-current MWGS reactor based on non-isothermal operation. The model was implemented in Aspen Plus and was written as a FORTRAN block.

This model determined the mass and energy balances for each component on both sides of the membrane. The permeation expression was based on linear pressure driving forces for the hydrogen fluxes (i.e. silica, zeolite and Pd-Alloy). However, as in the simplified model, the model did not take into account the temperature dependence of the permeance (i.e. the activation energy for the permeance was set equal to zero).

As mentioned earlier, the shift reaction is:

$$CO + H_2O \leftrightarrow H_2 + CO_2$$

The reaction is moderately exothermic (ΔH = -41.1 kJ/mol) and the equilibrium constant, K_p, is defined by:

$$K_p = \frac{C_{H_2} C_{CO_2}}{C_{CO} C_{H_2O}}$$

where C_i is the concentration of component I (mol/m^3). K_p decreases with increasing temperature so that higher temperatures produced less product. The equilibrium constant is defined as:

$$K_p = \exp\left(\frac{4577.8}{T} - 4.33\right)$$

The Fe-Cr catalyst was chosen as for the kinetic expression and the catalyst is active from 300°C to 450°C. The reaction rate was described using a power law expression:

$$R_{CO} = -k_1 C_{CO}^{0.73} C_{H_2O}^{0.55} \left(1 - \beta\right)$$

where β, the reversibility factor is defined as:

$$\beta = \frac{C_{CO_2} C_{H_2}}{K_p C_{CO} C_{H_2O}}$$

The model is based on the following assumptions:

- The membrane reactor is operated at non-isothermal, steady state conditions.
- The chemical reaction taking place on the feed side was homogeneously catalyzed.
- The catalyst is assumed to have no internal or external mass transfer limitations.
- The gases obeyed the ideal gas law.
- There is no pressure drop on the feed and permeate side of the membrane
- A flat plate membrane approach is used for the simulation of the MWGS reactor.
- The membrane is described as a single layer membrane with homoporous characteristics.
- Heat transport through the membrane is a combination of conduction and convection
- The temperature and concentration are only a function of the axial co-ordinate.
- Conduction and diffusion in axial direction are negligible compared to convection in axial direction.
- Heat effects as a result of possible decompression in the membrane are not taken into account.

Feed and sweep data (e.g. temperature, pressure, molar flows and physical properties (e.g. enthalpy, viscosity)) are directly transferred from Aspen Plus to the "user written" FORTRAN block that passes back the results directly back to Aspen Plus. Connecting streams are two inlet streams (feed and sweep streams) and two outlet streams (retentate and permeate streams).

Membrane and reaction specific input data was supplied in a separate data file (*.cfg) and as parameters in Aspen Plus (membrane surface area and ratio of feed volume to membrane surface area). The inputs in the *.cfg file that the user can change are:

- Switch for plug flow reactor versus membrane water gas shift reactor (switches off permeation capability)
- Switch between non-isothermal and isothermal operation
- Reaction rate constant for the shift reaction
- Reacting components in the shift reaction
- Stoichiometric coefficients for the shift reaction
- Power law coefficients for the reaction kinetics
- Permeating components
- Permeances of the individual components
- Heat transfer coefficient

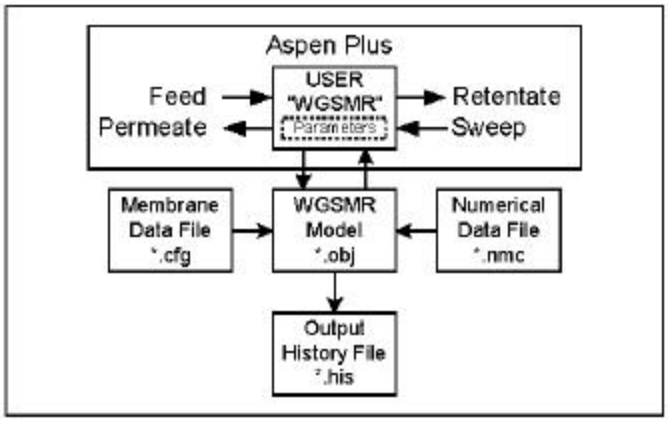
- Initial guesses for the retentate and permeate streams

Other input parameters are:

- Membrane type
- Flow type – counter-current
- Transport type – phenomenological transmembrane transport
- Number of components in the chemical reaction
- Reference temperature
- Activation energy for shift reaction
- Specific heat and enthalpy for components

In addition, numerical tuning parameters for the model are submitted in another data file (*.nmc). This *.nmc file is to remain unchanged by the user. The model output with membrane and reaction specific data is written to the Aspen Plus history file (*.his). The relationship between the different files are shown in Figure 3-7.

Figure 3-7
Membrane Model Interfaces



The default values and ranges for the input variables to the membrane model are shown Table 3-2.

Table 3-2 Default Values and Ranges for Input Variables		
Variable	**Default Value**	**Allowable Range**
Syngas feed temperature, °C	325	200 – 1000
Syngas feed pressure, bara	36	1 – 100
Sweep temperature, °C	325	200 – 1000
Sweep pressure, bara	24	1 – 100
Sweep flow rate, kmol/hr	18,400	None
Membrane surface area, m^2	2,200	None
Feed side catalyst volume/membrane surface area ratio, m^3/m^2	0.01	0.003 – 0.2

3.3.3 Final Version Simulation Model

The final version of the membrane model is similar to the first version simulation model; however, this model has the ability to estimate the performance for any membrane by the addition of an extra line to the *.cfg file for the exponent for the hydrogen flux equation. The model also included the temperature dependence of the permeance (i.e. the activation energy for the permeance was inputted as a value determined by the membrane vendors).

At the start of the programming effort for the final version, Colorado School of Mines/TDA stipulated that component fluxes had an exponential dependence on partial pressure (exponent = 0.515 to 0.845 for hydrogen and 1.05 for nitrogen). This dependence was chosen as it was discovered that the hydrogen diffused through the membrane as atomic hydrogen rather than molecular hydrogen (as in the silica and zeolite membranes).

In addition, the transport through the metal ceramic composite membranes had three contributions to the hydrogen flux as shown below.

1) Diffusion through the ceramic matrix (natural log pressure relationship)
2) Diffusion through the metal islands (exponential pressure relationship)
3) Diffusion through the ceramic-metal interfaces (Arrhenius type law for grain boundary diffusion)

It was stated by Eltron that the most important diffusion was item (2) – diffusion through the metal matrix; therefore, it was acceptable to ignore the other two types of diffusion for the hydrogen fluxes. The contribution due to item (1) only became significant when temperatures of the feed

exceeded 600°C (current temperature was 315°C). The contribution from item (3) was difficult to separate out and was accounted for in the permeance values provided by Eltron. In addition, the flux for the other components were essentially zero as long as there were no mechanical leaks present.

3.4 Membrane Simulation Model Results

3.4.1 Sensitivity Studies Results for First Version Membrane Simulation Model for the Silica Membrane

There are seven input variables to the first version membrane model and sensitivity runs were developed to determine the optimum operating conditions for the MWGS reactor to maximize carbon recovery. The sensitivity studies were based on the silica membrane as ECN had supplied the permeances for their membrane with the simulation model (permeances had not been received from the other vendors at this time). In addition, the First Version model was only applicable to the silica and zeolite membranes.

The sensitivity studies for the input variables were performed by setting the seven variables to the default values provided by ECN (shown in Table 3-2) and varying one variable at a time. These graphs provided a "starting" point for discussions among ECN, CCP and Fluor to determine the optimal operating conditions for the MWGS silica membrane reactor. Based on comments from ECN and CCP, recommended values were established for an optimal case.

The compositions for the pre-shifted syngas feed and sweep used for the sensitivity runs are shown in Table 3-3.

Table 3-3
Pre-shifted Syngas Feed and Sweep Compositions

Component	Pre-shifted Syngas Feed, mol%	Sweep, mol%
CH_4	155 ppmv	0
H_2O	33.7	0
CO_2	17.4	0
H_2	44.6	0
N_2	0.2	100.0
CO	4.0	0
H_2S	650 ppmv	0
COS	5 ppmv	0
NH_3	105 ppmv	0
Ar	280 ppmv	0
Total	100.0	100.0

The results from the membrane model were used to calculate the following parameters:

- Carbon Compounds = carbon in all carbon-containing compounds (i.e. CO, CO_2, CH_4 & COS)
- Carbon Recovery = (carbon compounds in retentate)/(carbon compounds in feed)
- Hydrogen Recovery = (H_2 in permeate)/(H_2 + CO in feed)
- CO_2 Purity = molar composition of CO_2 in retentate (mol%, dry basis)
- Permeate LHV = lower heating value of the hydrogen-rich fuel to the existing furnaces and boilers (permeate from the MWGS reactor).

(Source of definitions: "An Attractive Option for CO_2 Control in IGCC Systems: Water Gas Shift with Integrated H_2/CO_2 Separation (WIHYS) Process, Phase 1: Proof of Principle" by ECN dated December 1997).

The sensitivity studies were based on the default values provided by ECN and do not consider:

- physical constraints by the membrane (i.e. maximum differential pressure between the feed and permeate (100 bar from ECN) and maximum differential temperature between the feed and sweep (100°C from ECN))
- CCP's constraint on the CO_2 product purity (90 mol%, dry from CCP)
- CCP's constraint on the carbon recovery
- CCP's constraint on the permeate lower heating value (192 Btu/SCF (LHV) from CCP, which was later changed to 150 Btu/SCF (LHV) after consultation with furnace/boiler experts) (lower heating values which are too low may cause flame stability issues in the existing furnaces and boilers (even with modified burners)).

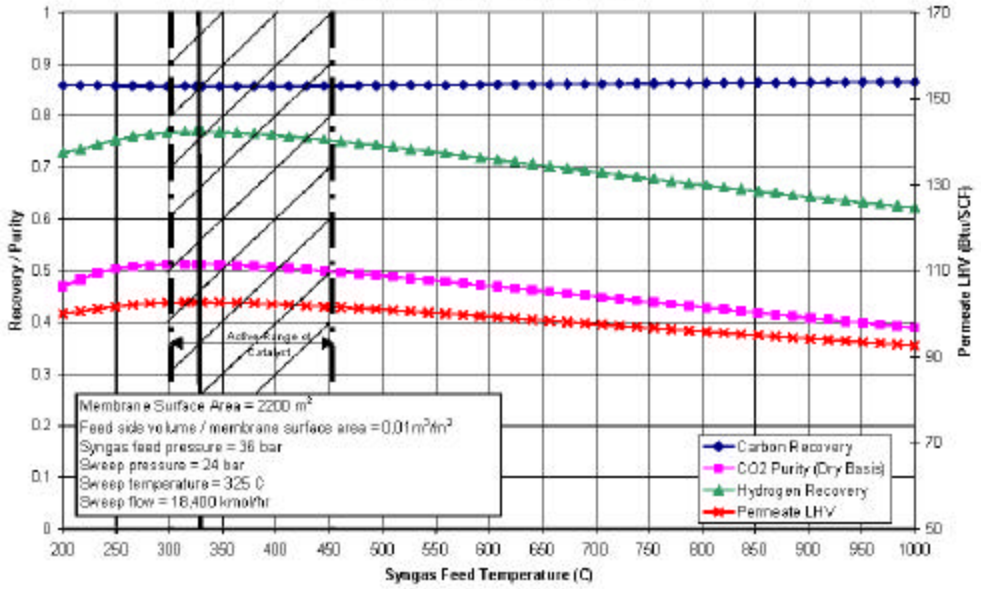
Note these sensitivity cases were based on the default values provided by ECN and did not include any optimization. Therefore, the graphs should be used to study the trends of the variables rather than absolute values. Also, the permeances were based on experimental data with sweet syngas (feed to the computer model is sour syngas).

The results of the computer model for the case with ECN's default values are shown in Table 3-4.

Table 3-4 Default Value Case Silica Membrane	
Carbon Recovery, %	85.8
Hydrogen Recovery, %	76.9
CO_2 Purity, mol% (dry)	51.3
Permeate LHV, Btu/SCF (LHV)	103

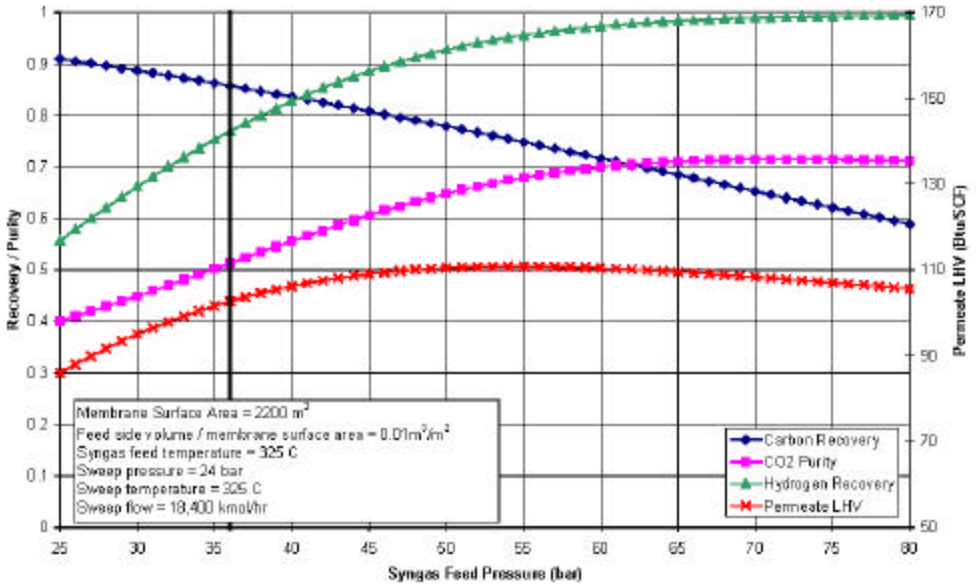
The Default Value Case is shown on the sensitivity graphs (Figures 3-8 to 3-14) as a vertical straight line for reference. Based on the sensitivity graphs and discussions among ECN, CCP and Fluor, conditions were chosen for the MWGS Reactor.

Figure 3-8
Syngas Feed Temperature Sensitivity
Silica Membrane - Default Values



As seen in Figure 3-8, the carbon recovery, carbon dioxide purity, hydrogen recovery and permeate LHV have relatively little change over the range of syngas temperatures studied. In fact, the four results are almost constant between the operating range of the catalyst (300°C to 450°C). (The catalyst chosen by ECN for the basis of the computer model was Iron-Chromium (Fe-Cr).) For the gasification plant, a lower syngas feed temperature increases the amount of steam that can be produced for power generation. Therefore, the syngas feed temperature was set close to the lowest temperature possible for the catalyst at 315°C (15°C margin was added to 300°C).

Figure 3-9
Syngas Feed Pressure Sensitivity
Silica Membrane - Default Values



As the syngas feed pressure increases (increasing driving force for hydrogen permeability), the carbon recovery decreases while the hydrogen recovery increases (at approximately twice the rate as that for the carbon recovery decrease) as shown in Figure 3-9. Basically, the results of the sensitivity study were inconclusive with no obvious maximum for carbon recovery and hydrogen recovery so the syngas feed pressure was set to 35 bara because a higher pressure favored the performance of the gasification plant.